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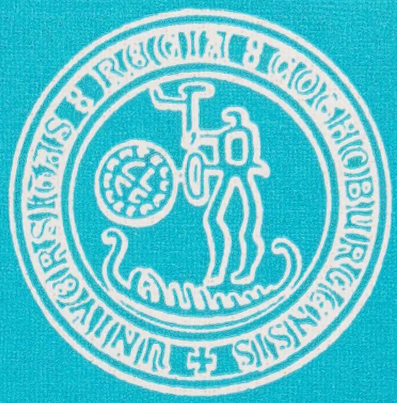

UNIVERSITY OF GOTHENBURG

INSTITUTIONEN FÖR OORGANISK KEMI
DEPARTMENT OF INORGANIC CHEMISTRY

Structure Analysis of Cubic and Tetragonal Forms of Telluric Acid and of Two Copper (II) Tellurates (VI)

Lennart Falck

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STRUCTURE ANALYSIS of CUBIC and TETRAGONAL FORMS of TELLURIC ACID and TWO COPPER(II) TELLURATES(VI)

Lennart Falck

AKADEMISK AVHANDLING

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STRUCTURE ANALYSIS of CUBIC and TETRAGONAL FORMS of TELLURIC ACID and TWO COPPER(II) TELLURATES(VI)

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This thesis is a resume' of the work presented in detail in the following papers:

I Lennart Falck, Oliver Lindqvist and Jacques Moret
"Tricopper(II)Tellurate(VI)"
Acta Cryst. (1978).B34, 896-897

II Lennart Falck, Oliver Lindqvist, Wanda Mark, Etienne Philippot and Jacques Moret
"The Crystal Structure of $CuTeO_4$"
Acta Cryst. (1978).B34,

III Lennart Falck and Oliver Lindqvist
"The Structure of Cubic $Te(OH)_6$"
In press

IV L. Falck, O. Lindqvist, J. Moret and J.L. Ribet
"The Synthesis and Crystal Growth of $Te(OH)_6 \cdot 4H_2O$
In press

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INTRODUCTION

At the commencement in 1965 of an investigation on the nature of the coordination in tellurium(VI) oxygen compounds at the Department of Inorganic Chemistry, Chalmers University of Technology and the University of Göteborg, very few structural reports were available on this subject (Lindqvist and Lundgren, 1966). The existence of three different phases of telluric acid was ascertained early (Berzelius 1834 and Mylius 1901), the monoclinic phase being the only one that is stable at room temperature. Its structure has been well established through X-ray (Lindqvist, 1970) and neutron diffraction (Lindqvist and Lehman, 1973) studies.

Cubic $Te(OH)_6$ was first investigated by single crystal X-ray methods by Kirkpatrick and Pauling (1926), who determined the space group and the unit cell dimensions. The space group is still valid but the author has found deviations in the cell parameters. Cohen-Addad (1971) investigated the cubic phase with the powder neutron diffraction technique and Mahalaxmi (1968) studied it with single crystal X-ray techniques. However, both these investigations are of rather low accuracy and it is not profitable to compare the results with those obtained for monoclinic $Te(OH)_6$.

The tetragonal phase $Te(OH)_6 \cdot 4H_2O$ was first reported by Berzelius (1834; 1835) and this phase , like the cubic phase, is unstable at room temperature. Bayer (1968) has reported an anhydrous tetragonal modification which may emanate from cubic $Te(OH)_6$. So far no single crystal X-ray or neutron diffraction studies have been made on this modification of telluric acid.

Structural reports on copper(II) tellurates(VI) are very limited in the literature. A powder X-ray investigation has been made of Cu_3TeO_6 (Coing-Boyat, 1968). Investigations on similar compounds include those on Mg_3TeO_6 (Schulz and Bayer, 1970) and Hg_3TeO_6 (Falqui, 1963) and a recent study of Ba_2CuTeO_6 (Köhle and Reinen, 1974).

No structural report is available on $CuTeO_4$ but there are some powder investigations on other $MeTeO_4$ phases (Me= Mg,Ca,Sr,Ba,Cd,Pb) (Sleight,Foris and Licis,1971), which give space groups and cell parameters. The structures of Na_2TeO_4 (Kratochvíl and Jenšovský,1977) and Li_2TeO_4 (Daniel, Moret, Philippot and Maurin,1977) are well established and contain chains of TeO_6 octahedra sharing edges.

The aim of the investigations presented in this thesis is to confirm and establish the regularity and the dimensions of the tellurium(VI)-oxygen octahedra in basic Te(VI) oxides in the solid state. Much effort has also been expended in the preparation of crystals of the unstable forms of telluric acid, i.e. $Te(OH)_6$ (cub.) and $Te(OH)_6 \cdot 4H_2O$, suitable for X-ray and neutron diffraction. A study of the detailed geometry of the $Te(OH)_6$ molecule in relation to the hydrogen bonds in the three different phases would constitute an unique opportunity of obtaining new information about the hydrogen bond. The other molecular hydroxy acid, $B(OH)_3$, is planar in the solid state with O-B-O angles of 120° (Zachariasen,1954; Craven and Sabine,1966), which does not give any information about the hydrogen bond.

PREPARATION OF THE CRYSTALS

The crystals have been prepared mainly by two methods, namely

hydrothermal synthesis and crystallization from aqueous solution at different temperatures.

Cu_3TeO_6

Crystals of Cu_3TeO_6 were prepared by hydrothermal synthesis. An aqueous solution of $CuSO_4$ (1M) and $Te(OH)_6$ (0.5 M) was held at 700 °C and 900 bar in an autoclave. After a week suitable single crystals of Cu_3TeO_6 were obtained. The crystals were deep green eclipsed octahedra. Microcrystals of $CuTeO_4$ were also formed and even some transparent TeO_2 crystals were formed under the above-mentioned conditions.

Crystals of $PbTeO_4$ have been prepared under similar conditions.

$CuTeO_4$

The preparation of crystals of $CuTeO_4$ could be improved by changing the hydrothermal conditions. If an aqueous solution of 0.5 M $CuSO_4$ and 0.5 M $Te(OH)_6$ was held at 650 °C and 2000 bar for two weeks, single crystals of Cu_3TeO_6, $CuTeO_4$ and a small amount of TeO_2 were again obtained simultaneously. The $CuTeO_4$ crystals which were obtained by this method were small yellow plates or irregular clusters. Slightly larger crystals could be obtained if the time for the hydrothermal synthesis was extended to two months and the concentration of $Te(OH)_6$ was increased to 1 M. In spite of the extended time of synthesis the crystals of $CuTeO_4$ were still very small and there were often cracks in the plates which made it difficult to find suitable single crystals.

$Te(OH)_6$ (cub)

Various methods for the preparation of cubic $Te(OH)_6$ are reported in

the literature (Bayer,1968). In the present work a saturated solution of $Te(OH)_6$ containing 20% acetic acid was prepared. The solution was evaporated rapidly at 70 °C. Many well shaped octahedra of cubic telluric acid were obtained. Crystals up to 0.3 mm were easily found; even crystals with an edge of 1.0 mm were observed but these were not completely transparent and were not suitable for the collection of neutron data.

Other methods of preparing large cubic $Te(OH)_6$ crystals have also been investigated:

A zone-melting apparatus was utilized and a sealed pyrex tube loaded with monoclinic $Te(OH)_6$ was used. The temperature of the heating coil of the equipment was about 160 °C. The speed of the coil was varied between 10-20 mm/hour. A well-formed seed of cubic $Te(OH)_6$ was also placed in the tube in order to try to induce growth of a large crystal. However, no single crystals were formed, probably because the temperature did not sink rapidly enough to prevent transformation back to the monoclinic phase.

Experiments with different temperature gradients were also performed. Sealed pyrex tubes containing powder of monoclinic $Te(OH)_6$ were placed in a furnace for 1-5 days and the gradient was varied between 7-14 °C/cm in the temperature range 60-200 °C. After the temperature gradient treatment, the furnace was turned off and was cooled to room temperature within three hours. An examination of the content did not show any cubic crystals.

The effect of quenching has not yet been investigated. Cubic crystals of $Te(OH)_6$ are assumed to be metastable at room temperature. However, it was found from several powder investigations, that if this phase

is allowed to age,the reflections split, indicating transformation to a tetragonal phase. This phase is probably the same as that reported by Bayer (1968), and a single crystal investigation will be performed.

$Te(OH)_6 \cdot 4H_2O$

When a solution of $Te(OH)_6$ is evaporated at temperatures below 60 °C, crystals of the stable monoclinic phase are formed. Even if the solution is saturated below 0 °C only the monoclinic phase crystallizes. To obtain crystals of the telluric acid hydrate, $Te(OH)_6 \cdot 4H_2O$, it is necessary to freeze a solution saturated at 0 °C to a low temperature, e.g. that of liquid N_2. The frozen mixture is then placed in another solution saturated at 0 °C, in which crystals of the hydrate then form It is thus possible that the tetragonal phase, being stable below 10 °C, has a considerable tendency to supersaturation but is formed as small nuclei in the frozen mass of $Te(OH)_6$ and water at low temperature. The dispersion of these nuclei in a $Te(OH)_6$ solution saturated at 0 °C will initiate rapid crystallization, since it is supersaturated with respect to $Te(OH)_6 \cdot 4H_2O$. When crystals of $Te(OH)_6 \cdot 4H_2O$ are available it is very easy to start the crystallization using seeds from a crushed crystal.

A detailed description of the preparation of seeds of the tetragonal $Te(OH)_6 \cdot 4H_2O$ phase, and the techniques used for growing large crystals (up to 1 cm^3) is given in Paper IV.

CRYSTALLOGRAPHIC METHODS

Some physical properties of the phases investigated are given in Table 1.

Preliminary space groups and cell dimensions were determined from

Table 1. Some physical properties for the different phases of telluric acid.

	$Te(OH)_6$mon	$Te(OH)_6$cub	$Te(OH)_6 \cdot 4H_2O$
Density	3.07 g cm^{-3}	3.16 g cm^{-3}	2.40 g cm^{-3}
Stability	stable at $T<60$ °C	stable at $60<T<136$ °C	stable at $T<10$ °C
Solubility	410 g l^{-1} at $T=25$ °C	-	220 g l^{-1} at $T=4$ °C
Melting point	136 °C	136 °C	-

Weissenberg films. Improved cell parameters (cf. Table 2.) were obtained from Guinier powder photograms taken with $Pb(NO_3)_2$ as an internal standard ($\underline{a}$=7.8566 Å at 21 °C). The Guinier camera was first adjusted so that a splitting of $Cu\underline{K}\alpha_1$ and $Cu\underline{K}\alpha_2$ was obtained in the primary beam.

Intensity data (cf. Table 3) were collected for Cu_3TeO_6 and $CuTeO_4$ on a two-circle PAILRED diffractometer. Graphite monochromated $Mo\underline{K}\alpha$ radiation was used and intensities were measured with the ω-scan procedure with a scan speed of 2.5 ° min^{-1}. The scan interval was 2-3° and the background was measured for 24 sec. at each end of the scan interval. Only reflections with $\sigma(I)/I<0.3$ were registered. The layers $\underline{h}\ \underline{k}\ 0$ - $\underline{h}\ \underline{k}\ 12$ ($\underline{k} \geq 0$) were explored for Cu_3TeO_6, and $\underline{h}\ 0\ \underline{l}$ - $\underline{h}\ 9\ \underline{l}$ out to $2\theta = 60°$ for $CuTeO_4$.

The X-ray intensity data for $Te(OH)_6$ and $Te(OH)_6 \cdot 4H_2O$ were collected on a four-circle SYNTEX $P2_1$ diffractometer using graphite monochromated $Mo\underline{K}\alpha$ radiation. A $\omega/2\theta$ scan was used with scan intervals of 2.4-3.2° ($\Delta\ 2\theta$), the scanning speed being varied between 2.0-12.0° min^{-1}. Intensities were measured out to $2\theta \sim 60°$ and reflections with $I/\sigma(I) \geq 3$ were used in the refinement of the structure. For cubic $Te(OH)_6$, one eighth of the reciprocal space was registered, corresponding to a six-fold redundancy, since the reflections ($\underline{h}\ \underline{k}\ \underline{l}$), ($\underline{l}\ \underline{h}\ \underline{k}$), ($\underline{k}\ \underline{l}\ \underline{h}$), ($\underline{h}\ \underline{l}\ \underline{k}$), ($\underline{k}\ \underline{h}\ \underline{l}$) and ($\underline{l}\ \underline{k}\ \underline{h}$) are symmetry-related in space group Fd3c. Cubic $Te(OH)_6$ is not, however, stable to X-ray radiation, and the intensity of the standard reflection dropped by 30% during the data collection (58 h exposure); cf. Fig. 1. It was therefore not considered profitable to average the symmetry-related reflections, and the unique data set measured first was used in the calculations.

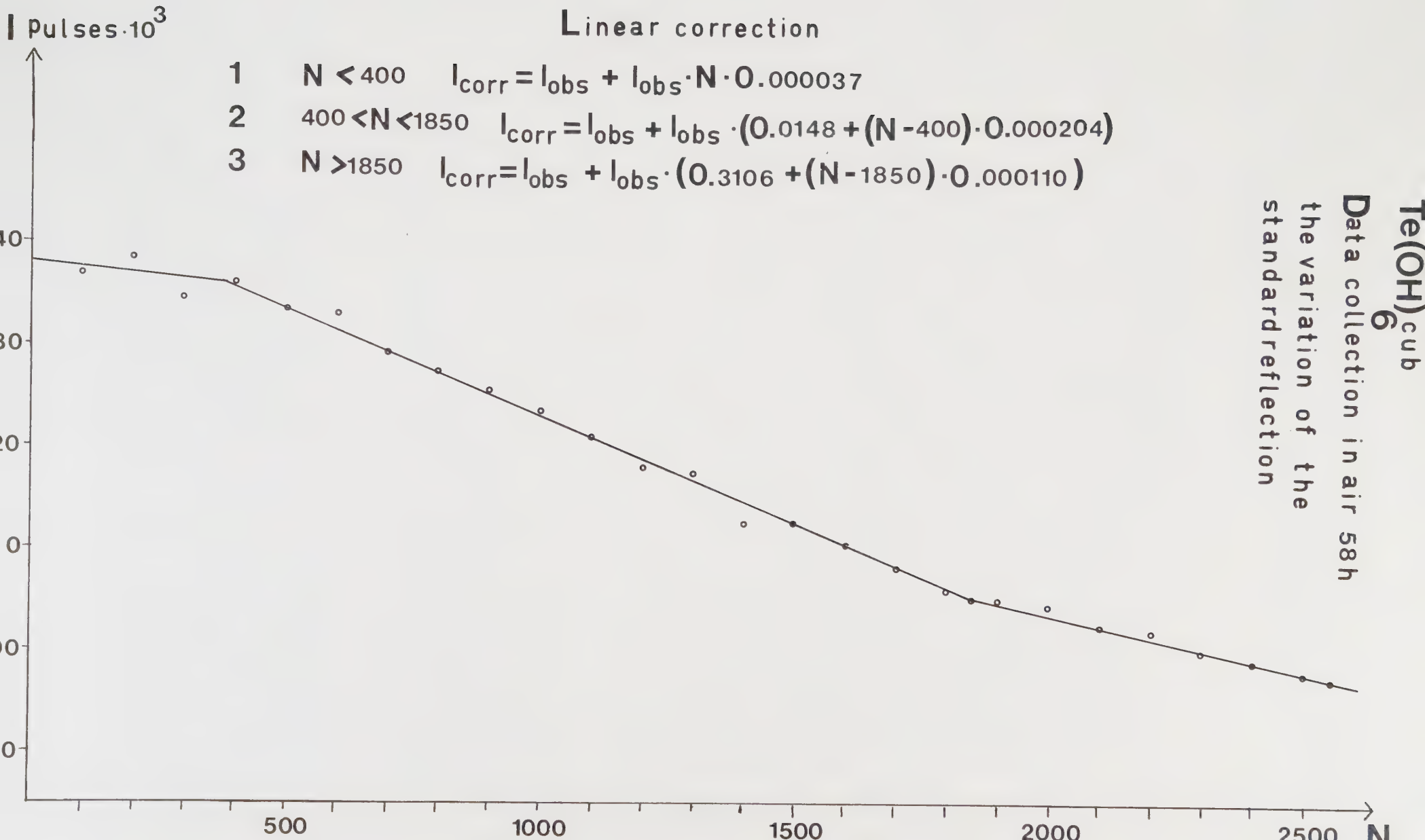
Table 2. Unit cell dimensions

Compound	Space group	a	b	c	β	V	z
Cu_3TeO_6	Ia3	9.537(1)	-	-	-	867.2(2)	8
$CuTeO_4$	$P2_1/n$	5.500(2)	10.327(7)	4.704(2)	90.0(1)	267.2(3)	4
$Te(OH)_6$cub.	Fd3c	15.705(2)	-	-	-	3873.6(5)	32
$Te(OH)_6$tet.	-	15.652(5)	-	15.762(5)	-	3861.5(8)	32
$Te(OH)_6 \cdot 4H_2O$	$I4_1/a$	10.790(4)	-	7.108(3)	-	827.5(5)	4

Table 3. Intensity data

Compound	Data collection procedure	Radiation	Crystal dimensions (mm)	Setting	No of reflections	R-value	μ_λ cm^{-1}	Gaussian grindes	Transmission ranges
Cu_3TeO_6	Philips PAILRED 2-circle diffractometer	MoKα (mon)	0.13x0.10x0.13	[100]	1543	2.2	218.9	6x6x6	0.14-0.22
$CuTeO_4$	"	"	0.03x0.001x0.10	[101]	401	4.8	193.6	4x4x6	0.72-0.92
$Te(OH)_6$cub	Syntex $P2_1$ four-circle diffractometer	"	0.20x0.20x0.20	A	484	2.5	62.1	4x4x4	0.57-0.62
$Te(OH)_6 \cdot 4H_2O$ X-ray	"	"	0.40x0.20x0.10	A	672	8.3	60.8	-	-
$Te(OH)_6 \cdot 4H_2O$ neutron	Hilger & Watts four circle diffractometer	1.21 Å (mon)	7x4x2	A	1650	21.4	2.7	-	-

FIG 1.


I Pulses·10³
Linear correction
1 N < 400 $I_{corr} = I_{obs} + I_{obs} \cdot N \cdot 0.000037$
2 400 < N < 1850 $I_{corr} = I_{obs} + I_{obs} \cdot (0.0148 + (N - 400) \cdot 0.000204)$
3 N > 1850 $I_{corr} = I_{obs} + I_{obs} \cdot (0.3106 + (N - 1850) \cdot 0.000110)$
40
30
20
0
00
0
500
1000
1500
2000
2500
N
Te(OH)6 cub
Data collection in air 58 h
the variation of the
standard reflection

The methods used to solve the structures are described in the separate papers on Cu_3TeO_6, $CuTeO_4$ and $Te(OH)_6$ (cub), while the work on $Te(OH)_6 \cdot 4H_2O$ is described in more detail here.

$Te(OH)_6 \cdot 4H_2O$; X-ray diffraction investigation

A crystal of suitable size (cf. Table 3.) was mounted with epoxy adhesive in a capillary. Crystal growth (cf. Paper IV) and mounting work were performed at +4 °C. The mounted crystal was transferred to the SYNTEX $P2_1$ diffractometer which was operated with the Syntex low temperature device (LT-1). This is usually run with liquid N_2 moderated to a desired temperature with a gas stream heater. However, in this data collection the heating and N_2 refill automatics were disconnected and the cooling device was used with ice and compressed air from the main line in the chemistry building. The temperature of +2°C thus obtained was suitable for keeping the $Te(OH)_6 \cdot 4H_2O$ crystal stable in the capillary.

The diffractometer settings, as well as some physical and crystallographic data for $Te(OH)_6 \cdot 4H_2O$ are summarized in Table 4.

The integrated intensities and $\sigma(I)$ values were obtained from a profile analysis of the step-scanned reflections according to the Lehman-Larsen (1974) method. The data were corrected for Lorentz and polarization effects using the local program SYN, but as yet no correction has been made for absorption.

Weissenberg films 0 $\underline{k}$ $\underline{l}$ - 2 $\underline{k}$ $\underline{l}$ and $\underline{h}$ $\underline{k}$ 0 - $\underline{h}$ $\underline{k}$ 2 have been collected to establish the symmetry of the crystals, the reflection symmetry and the systematic absences uniquely indicating the space group to be $I4_1/a$ Some of the films were over exposed to check if any continuous intensity distribution ($\underline{i.e.}$ indicating OD character) was present, but no such

Table 4. Experimental and physical data.

1. Physical and crystallographic data

Formula:	$Te(OH)_6 \cdot 4H_2O$	a = 10.790(4) Å
Molecular weight:	301.64	b = 10.790(4) Å
Space group:	$I4_1/a$	c = 7.108(3) Å
Absorption:	60.8 cm^{-1}	V = 827.5(5) $Å^3$
Density:	2.40 g cm^{-3}	
Crystals:	Colourless parallellepideds stable below +10 °C	

2. Data collection (X-ray)

Crystal dimension:	0.40 x 0.20 x 0.10 mm^3
Radiation:	MoKα = 0.71069 Å
Monochromator:	Graphite crystal
Scan mode:	ω/2θ
Maximum 2θ angle:	60.0°
Scan interval:	Δ2θ 2.4°-3.2°/min
Scan speed (in 2θ):	1.0°/min - 12.0°/min
Standard reflection:	004, 152, 512 in intervals of 25
Recorded reflections:	672, no time variation
Significant reflections:	512
Temperature:	+2 °C
Cooling equipment:	LT-1

phenomena were observed (cf. Fig. 2). The symmetry was further investigated on the diffractometer, and the reciprocal space was explored for all reflections with $0 \leq \underline{h} \leq 3$, $-3 \leq \underline{k} \leq 3$, $-3 \leq \underline{l} \leq 3$. No deviation from $I4_1/a$ symmetry was indicated. The data collection was performed as if the crystal were monoclinic, i.e. a two-fold redundancy was obtained. A small computer program was written to analyze the agreement between symmetry-related reflections, and it was found that $R(sym,I) = |I_{hkl} - I_{k\bar{h}l}|/I_{hkl} = 0.09$ and $R(sym,F) = 0.045$. These values are reasonable and due to lack of correction for absorption and to statistical effects.

The positions of the tellurium atoms were evident ($I4_1/a$: 4(a)) due to the fact that there are four formula units of $Te(OH)_6 \cdot 4H_2O$ in the unit cell. The oxygen atomic positions were then easily obtained from an electron density summation, and the structure was refined to an R-value of 0.083. The corresponding atomic coordinates and isotropic temperature factors are given in Table 5.

It has not yet been possible to apply any successful absorption correction, although the morphology of $Te(OH)_6 \cdot 4H_2O$ is well established (Paper IV). In a refinement using anisotropic temperature factors and the symmetry of space group I2/a an R-value of 0.061 was obtained. Assuming that the inclusion of anisotropic temperature factors may compensate for most of the absorption errors, this R-value is relatively high compared with similar structures for which data has been collected with the SYNTEX $P2_1$ diffractometer. Although the structure model, as shown in Table 5., is reasonable, and although there is no residual electron density corresponding to any atomic positions, it is possible that the present model is not exactly correct.

Fig. 2 Weissenberg films of $Te(OH)_6 \cdot 4H_2O$, Mo$\underline{K}\alpha$ (mon) radiation, exposure 25-50 h.

Fig. 2a 0 $\underline{k}$ $\underline{l}$ $\underline{a}$= 10.79 Å

Fig. 2b 1 $\underline{k}$ $\underline{l}$

Fig. 2c $\underline{h}$ $\underline{k}$ 0 $\underline{c}$ = 7.11 Å

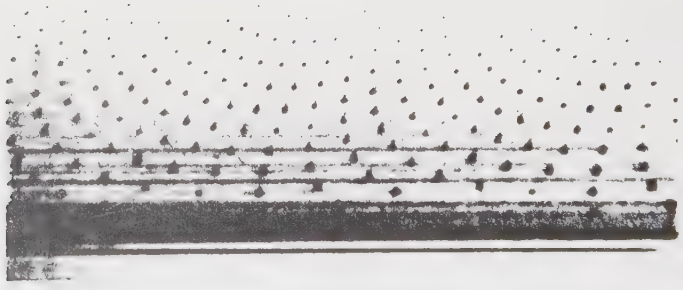


Fig. 2d $\underline{h}$ $\underline{k}$ 1

Table 5. Atomic coordinates and isotropic temperature factors (B $Å^2$) for $Te(OH)_6 \cdot 4H_2O$ (X-ray investigation)

	x	y	z	B
Te	0	1/4	1/8	0.26(3)
O_1	0	1/4	0.397(2)	1.5(3)
O_2	0.052(1)	0.425(1)	0.124(2)	1.6(2)
O_3	0.128(1)	0.055(1)	0.563(2)	1.2(2)

$Te(OH)_6 \cdot 4H_2O$; neutron diffraction investigation

To ascertain the hydrogen positions in the structure a suitable single crystal was grown by methods mentioned in Paper IV. A crystal (7x4x2 mm^3) was mounted in a silica tube with epoxy adhesive. The neutron diffraction data were collected with a computer-controlled Hilger & Watts four-circle diffractometer at the Swedish Atomic Energy reactor R2 at Studsvik. A doubly monochromated neutron beam (Stedman, Almqvist, Raunio and Nilsson, 1969) of wave length 1.210 Å was used and the measurements were performed in a $\omega/2\theta$ step scan mode with steps of $1/20^o$ and scan intervals of 2^o.

Because of the instability of the $Te(OH)_6 \cdot 4H_2O$ crystal a cooling equipment was used for the data collection. In this cooling system $N_2(g)$, cooled in $N_2(l)$, is constantly blown on to the silica tube containing the crystal. The cooled N_2 stream could be heated so that a temperature of +2 ^oC was obtained. To prevent accidental ice-growth on the nozzle a resistant wire (Kanthal) was wound around the outermost part of the gas nozzle and a small electrical current was applied. This simple construction prevented the nozzle from being filled with ice.

The reflection profiles were obtained in 40 steps each being measured for 6 sec. This relatively high speed was considered suitable since the reflections were narrow and the crystal size was optimum, i.e. ~ 50 mm^3 for $Te(OH)_6 \cdot 4H_2O$. The data were obtained on magnetic tape and the standard profile analysis program (LELA) (cf. Table 6.) was modified to directly read the Studsvik data tape, and to handle a 40 step scan instead of a 96 step scan. The performance of the modified LELA program was checked carefully. A total of 1650 symmetry-related $\underline{h}\ \underline{k}\ \underline{l}$ and $\underline{k}\ \underline{h}\ \underline{l}$ reflections were obtained out to $\sin\theta/\lambda = 0.80$ $Å^{-1}$. All reflections

Table 6. Applied data programs.

Calculation	Program	Authors
Refinement of cellparameters	POWDER	O. Lindqvist F. Wengelin (1967)
Bond and angle calculation	DISTAN	Zalkin, Berkely Carlifonia
LP-correction	DATAP1	O. Lindgren (1977)
Absorption corrections	DATAPH	Coppens, Leiserowitz and Rabinovich (1965)
Fourier Summation	DRF	Zalkin, Berkely Carlifornia
Least square refinements (block-diagonal)	BLOCK	Lindgren (1977)
Fullmatrix-refinements	LINUS	Coppens and Hamilton (1970)
Lehman-Larsen profile-analysis	LELA	Lindqvist and Ljungström (1977)
Drawings	ORTEP	Johnson (1965)

within $\sin\theta/\lambda < 0.2$ Å^{-1} were measured in order to confirm the space group symmetry, i.e. $I4_1/a$. There were no evident deviations from this symmetry, but the R (sym,F) value, based on all significant reflections ($I>3\sigma(I)_{count}$) was 0.09. However, this high value is probably mainly due to absorption effects.

A preliminary refinement (LINUS; Coppens and Hamilton, 1970) based on the tellurium and oxygen parameters obtained in the X-ray work gave an R-value of 0.32 when isotropic temperature factors were used. A Fourier summation with signs based on this model revealed very sharp peaks corresponding to the tellurium and oxygen atomic positions, but the negative peaks indicated that the hydrogen atoms were disordered in $I4_1/a$. From chemical considerations it is highly unlikely that the hydrogen atom attached to O_1 can conform to the ordered $I4_1/a$ structure, since this would imply a linear H_{11}-O_1-Te-O_1-H_{11} arrangement on a two-fold axis. Even if the symmetry is lowered to I2/a this arrangement is obtained, and one would have to consider Ia as the only plausible space group for a fully-ordered structure. Several cycles of refinement and Fourier calculations based on plausible hydrogen positions have been performed. At present the best model is obtained in space group $I4_1/a$ with disordered hydrogen positions.

This model is shown in Table 7 and includes all the hydrogen atoms. The temperature factors are reasonable and the occupation numbers have been obtained from an earlier refinement in which the temperature factors were fixed for all the hydrogen atoms to a value of 2.1 Å^2. However, the R-value is as poor as 0.21, which is far worse than expected from lack of correction for absorption and extinction effects.(Similar R-values were obtained for different refinements in space group Ia).

Table 7. Atomic coordinates and isotopic temperature factors (B $Å^2$) for $Te(OH)_6 \cdot 4H_2O$ (neutrons diffraction study)

	x	y	z	B $Å^2$	occup. numbe
Te_1	0.00	0.25	0.125	1.2(3)	0.25
O_1	0.00	0.25	0.398(2)	2.2(2)	0.50
O_2	0.0539(7)	0.4197(7)	0.124(1)	2.2(2)	1.00
O_3	0.1238(8)	0.0547(7)	0.565(1)	1.9(2)	1.00
H_{11}	0.972(3)	0.294(3)	0.450(4)	2.4(4)	0.50
H_{21}	0.062(3)	0.437(3)	0.252(6)	2.9(6)	0.40
H_{22}	0.007	0.461(2)	0.047(3)	2.6(4)	0.60
H_{31}	0.093(4)	0.031(4)	0.648(7)	3.7(7)	0.40
H_{32}	0.152(2)	0.007(2)	0.467(2)	3.2(4)	0.80
H_{33}	0.037(4)	0.097(4)	0.522(7)	5.1(9)	0.40
H_{34}	0.180(4)	0.089(4)	0.645(7)	4.4(8)	0.40

R value = 0.21

The quality of the data (R(sym,F)=0.09 before absorption and extinction corrections) indicates that it ought to be possible to find a relevant model. Possible OD structures, in which the disorder only affects the hydrogen positions will be considered and further work will be performed in space group Ia.

DESCRIPTION OF THE STRUCTURES

Detailed descriptions of the structures are to be found in Papers I-III and only the main structural features will be described in this section. Selected interatomic distances are listed in Table 8.

I Cu_3TeO_6

Cu_3TeO_6 contains TeO_6 octahedra connected by copper(II) atoms (cf.Fig.3). T tellurium atom is situated on a three-fold inversion axis and the bonding orbitals have the symmetry C_{3i}. The copper atoms are surrounded by a distorted octahedral configuration of oxygen atoms. The interaction between copper and oxygen is mainly ionic, the structure thus being built up from TeO_6^{6-} and Cu^{2+} ions. The Te-O bonds are 1.921(2) Å (6x) and the O-Te-O angle generated by the three-fold rotation is 94.2°(1).

II $CuTeO_4$

The structure consists of Cu^{2+} ions and infinite $[TeO_4]_n^{2n-}$ layers of TeO_6 octahedra sharing corners. There are two chemically equivalent ways of stacking these layers. It is therefore useful to describe the

Table 8. Selected distances and angles in the structures investigated.

	Te-O	O-Te-O	
Cu_3TeO_6	1.921(2) Å (6x)	94.0°(1)	
$CuTeO_4$	1.87(2)-2.02(2) Å	84.2(9)-99.2°(8)	
$Te(OH)_6$cub	1.913(6) Å (6x)	90.2°(3)	
$Te(OH)_6 \cdot 4H_2O$	1.921(8) Å (4x) 1.938(12) Å (2x)	90.1°(3)	(neutrons)
	1.97(2) Å (4x) 1.93(2) Å (2x)	90.2°(4)	(X-rays)

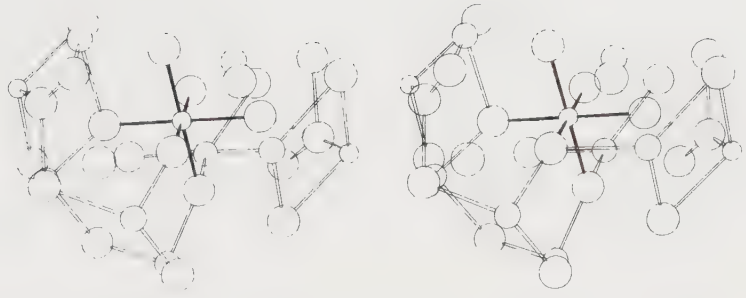


Fig. 3. A stereoscopic picture of Cu_3TeO_6 projected along the c-axis. (ORTEP; Johnson, 1965)

structure in terms of two models MDO_1 and MDO_2. The OD character is discussed in detail in Paper II. (cf. Fig. 4)

III $Te(OH)_6$ (cub)

The cubic modification of telluric acid is built up of isolated octahedral $Te(OH)_6$ molecules. The Te-O bonds are 1.913(6) Å (6x) and the O-Te-O angle 90.2°(3). These almost regular octahedra are connected by hydrogen bonds, each octahedron being involved in twelve hydrogen bonds. (cf. Fig.5)

IV $Te(OH)_6 \cdot 4H_2O$

The structural results on $Te(OH)_6 \cdot 4H_2O$ have not yet been published due to the fact that the positions of the hydrogen atoms are not yet fully resolved. However, the tellurium and oxygen arrangement would appear to be correct and the results are summarized in Table 9, including data from both the X-ray and the neutron diffraction studies. This table also includes some distances and angles involving hydrogen atoms whose positions have been refined to plausible values. The octahedral Te-O bond distances are 1.93-1.97 Å, and the O-Te-O bond angles are 90° within the standard deviations. Each $Te(OH)_6$ molecule is hydrogen-bonded to eight different water molecules, while there are four hydrogen bridges directly linking $Te(OH)_6$ molecules. Each water molecule is involved in four hydrogen bonds. (cf. Fig. 6)

DISCUSSION

All known structures of tellurates(VI) exhibit octahedral coordination of the hexa-valent tellurium atom by oxygen. The coordination polyhedron

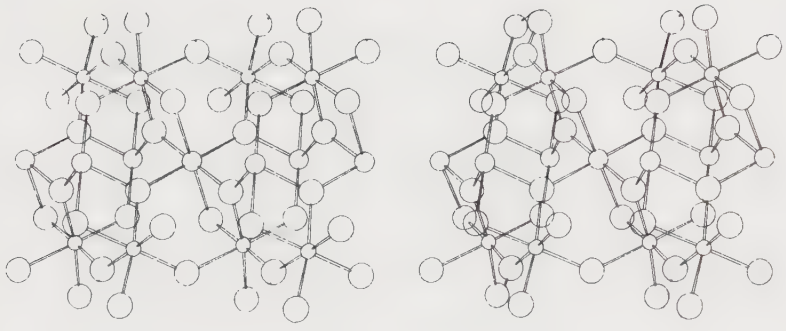


Fig.4. A stereoscopic picture of $CuTeO_4$ projected along the c axis (ORTEP; Johnson, 1965).

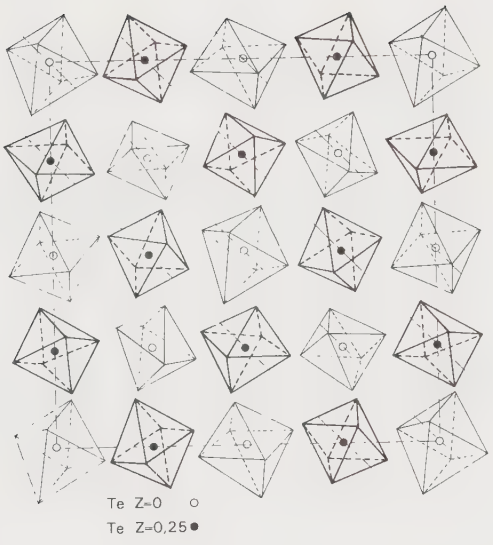


Fig. 5. A schematic picture of $Te(OH)_6$ cub. (Moret,Philippot,Maurin and Lindqvist, 1974).

Table 9. Bond distances and angles in $TeO_6 \cdot 4H_2O$.

a) X-ray diffraction investigation

Te-O	O----O	O-Te-O
1.93(2)Å (2x) 1.97(2)Å (4x)	2.65(3)-2.78(2)Å	89.8(4)-90.2°(4)

b) Neutron diffraction investigation

Te-O	O-Te-O
1.938(12)Å (2x) 1.921(8)Å (4x)	89.9°(3)-90(1)°(3)

Table 9. Continued

O---O		O-H---O		O-H		O---H	
O_1---O_3	2·765(10) Å	O_1-H_{11}---O_3	169(3)°	O_1-H_{11}	0.67(3) Å	O_1---H_{33}	1.91(5) Å
O_2---O_2	2.736(18) (2x)	O_3-H_{33}---O_1	132(3)°	O_2-H_{21}	0.93(4)	O_2---H_{22}	1.89(2)
O_2---O_3	2.748(13) (2x)	O_2-H_{22}---O_2	163(2)°	O_2-H_{22}	0.87(2)	O_2---H_{31}	2.05(5)
O_3---O_3	2.750(9) (2x)	O_2-H_{21}---O_3	145(3)	O_3-H_{31}	0.72(5)	O_3---H_{11}	2.10(3)
		O_3-H_{31}---O_2	160(4)	O_3-H_{32}	0.92(2)	O_3---H_{21}	1.93(4)
		O_3-H_{32}---O_3	163(2)	O_3-H_{33}	1.08(5)	O_3---H_{32}	1.85(2)
		O_3-H_{34}---O_3	168(4)	O_3-H_{34}	0.90(5)	O_3---H_{34}	1.85(5)

Te-O-H		Te-O---H		H-O---H	
Te-O_1-H_{11}	123°(2) (2x)	Te-O_1---H_{33}	117°(1) (2x)	H_{11}-O_1---H_{33}	116°(3) (2x)
Te-O_2-H_{21}	102°(2)	Te-O_2---H_{31}	128(1)	H_{21}-O_2---H_{22}	121(2)
Te-O_2-H_{22}	108(2)			H_{22}-O_2---H_{31}	108(2)
				H_{31}-O_3---H_{11}	111(3)
				H_{32}-O_3---H_{11}	107(2)
				H_{34}-O_3---H_{11}	104(3)
				H_{32}-O_3---H_{21}	104(2)
				H_{33}-O_3---H_{21}	99(3)
				H_{34}-O_3---H_{21}	94(3)
				H_{31}-O_3---H_{34}	112(4)
				H_{32}-O_3---H_{32}	108(2)
				H_{33}-O_3---H_{32}	136(3)
				H_{33}-O_3---H_{34}	107(3)
				H_{34}-O_3---H_{34}	123(4)

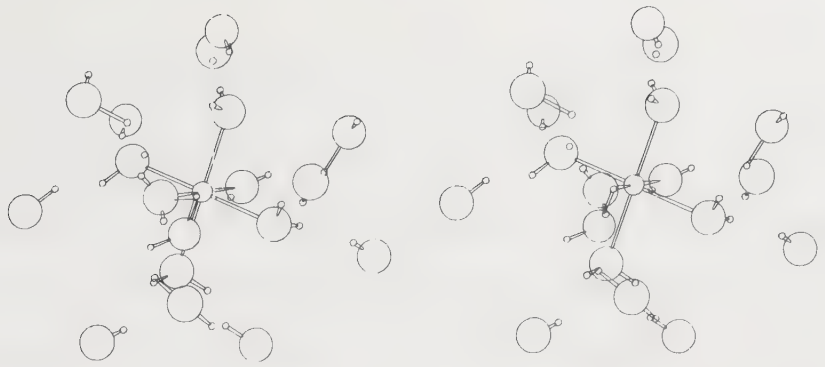


Fig. 6 a). A stereoscopic picture of $Te(OH)_6 \cdot 4H_2O$ projected along the c axis (ORTEP; Johnson, 1965).

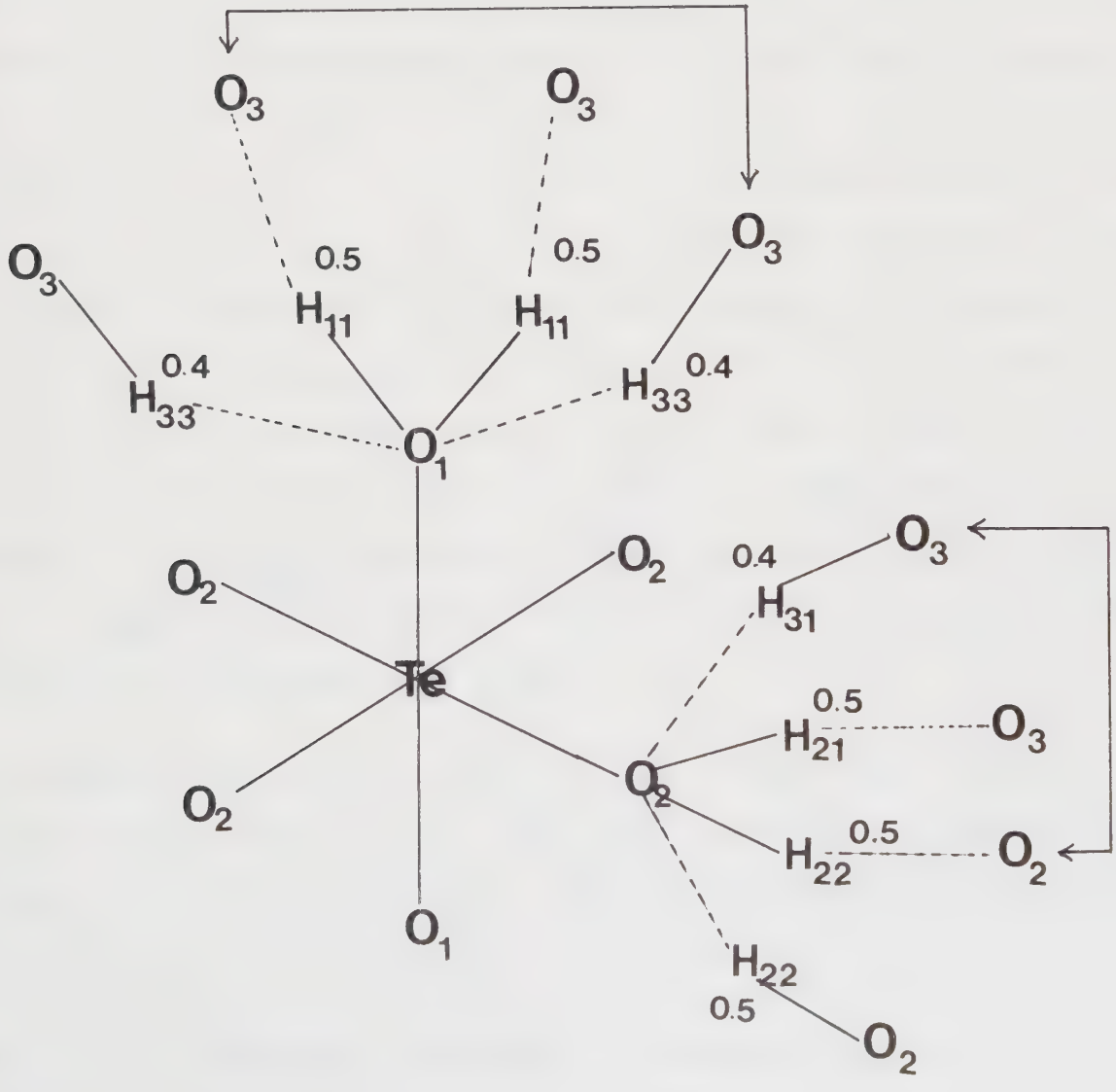


Fig. 6 b). An indication of the disordered hydrogen bonds in accordance with Table 9. Occupation numbers are indicated.

may be more or less distorted. The most regular TeO_6 arrangement is found in cubic telluric acid (Paper III) in which the Te-O distances are all 1.913(6) Å due to the crystallographic six-fold $\bar{3}$ symmetry and the O-Te-O angles do not deviate significantly from 90°. The distortions found in monoclinic telluric acid (Lindqvist and Lehman, 1973), the stable form at room temperature, are rather small, the Te-O distances being 1.907(1)-1.914(1) Å and the O-Te-O angles 87.60(6)-92.08(7)°. These slight deviations from perfect octahedral symmetry reflect the effects of hydrogen bonding in the monoclinic structure.(cf. Table 10)

Larger distortions are observed in tellurates(VI) in which the $Te(OH)_6$ molecules are dissociated and condensed (Fig.7 and Fig.8).The Te-O bond distances may here be classified as hydroxyl, bridging or terminal, according to the role of the oxygen atom. The greatest deviations from octahedral symmetry are expected to lie within the range 1.80 Å (shortest terminal Te-O distance) - 2.05 Å (longest bridging Te-O distance). For example, a $Te\text{-}O_{terminal}$ bond length of 1.83(2) Å has been found in $KTe(OH)_5 \cdot H_2O$ (Raman, 1965) and a $Te\text{-}O_{bridge}$ bond of 2.04(1) Å in $Na_2K_4[Te_2O_8(OH)_2] \cdot 14H_2O$ (Lindqvist, 1969). In $CuTeO_4$ (Paper II) there is a $Te\text{-}O_{bridge}$ distance of 2.02(2) Å. One of the most distorted O-Te-O angles, 77.9(1)°, has been found in $KTeO_3(OH)$ (Lindqvist, 1972) in which two octahedra share an edge.

The oxygen coordination of Te(VI) may thus be summarized: Octahedral with a Te-O distance of 1.91 Å, Te-O bonds in distorted octahedra lying within the range 1.80-2.05 Å, the maximum angular deviation from the expected value of 90° being 15°.

Three of the compounds investigated are monomeric tellurates(VI) (cf. Fig. 7a), namely cubic telluric acid $Te(OH)_6$, tetragonal telluric acid

Table 10. Bond distances in some compounds containing $Te(OH)_6$ molecules.

Compound	Te-O Å	O-Te-O°	O ---- O Å	ref.
$Te(OH)_6$ mon X-ray study	1.905(5) 1.911(5) 1.918(5) 1.918(4) 1.925(5) 1.916(5)	87.8(2) 89.1(2) 91.6(2) 89.0(2) 91.6(2) 92.2(2)	2.681(7) 2.696(7) 2.694(7) 2.687(7) 2.687(7) 2.728(7)	Lindqvist (1970)
Te(OH) mon neutron study	1.907(1) 1.908(1) 1.910(1) 1.908(1) 1.908(1) 1.914(1)	88.69(7) 91.07(6) 92.08(7) 87.60(6) 88.38(6) 90.71(7)	2.695(2) 2.707(2) 2.696(2) 2.685(2) 2.676(2) 2.730(2)	Lindqvist and Lehman (1973)
$Te(OH)_6$ cub	1.916(3) (6x)	90.2(3)	2.639(12) (3x) 2.773(13) (3x)	Paper III
$Te(OH)_6 \cdot 4H_2O$	1.921(8) (4x) 1.938(12) (2x)	90.1(9)	2.750(9) (2x) 2.765(10) 2.736(18) (2x) 2.748(13) (2x)	
$Te(OH)_6 \cdot 2KF$	1.902(4) (2x) 1.903(4) (2x) 1.911(4) (2x)	91.6	2.573(5) * 2.590(5) * 2.605(5) *	Allmann and Haase (1976)
$Te(OH)_6 \cdot NaF$	1.91(1) (3x) 1.92(1) (3x)	-	2.76(2) 2.50(2) *	Allman (1976)

* O ..... F distance

Fig. 7 Schematic diagram of tellutate(VI) anions, which may be formed by the dissociation and/or condensation of telluric acid. Probable structure types are indicated in Fig.8. (Lindqvist, 1973)

Dissociation	Condensation → $-H_2O$	$-2H_2O$	$-3H_2O$
$-H^+$	$Te(OH)_6$	$TeO(OH)_4$	$TeO_2(OH)_2$	TeO_3
$-2H^+$	$TeO(OH)_5^-$	$TeO_2(OH)_3^-$	$TeO_3(OH)^-$	
$-3H^+$	$TeO_2(OH)_4^{2-}$	$TeO_3(OH)_2^{2-}$	TeO_4^{2-}	
$-4H^+$	$TeO_3(OH)_3^{3-}$	$TeO_4(OH)^{3-}$		
$-5H^+$	$TeO_4(OH)_2^{4-}$	TeO_5^{4-}		
$-6H^+$	$TeO_5(OH)^{5-}$			
	TeO_6^{6-}			
Probable structure type:	Fig. 8a	b, c	d, e	ReO_3

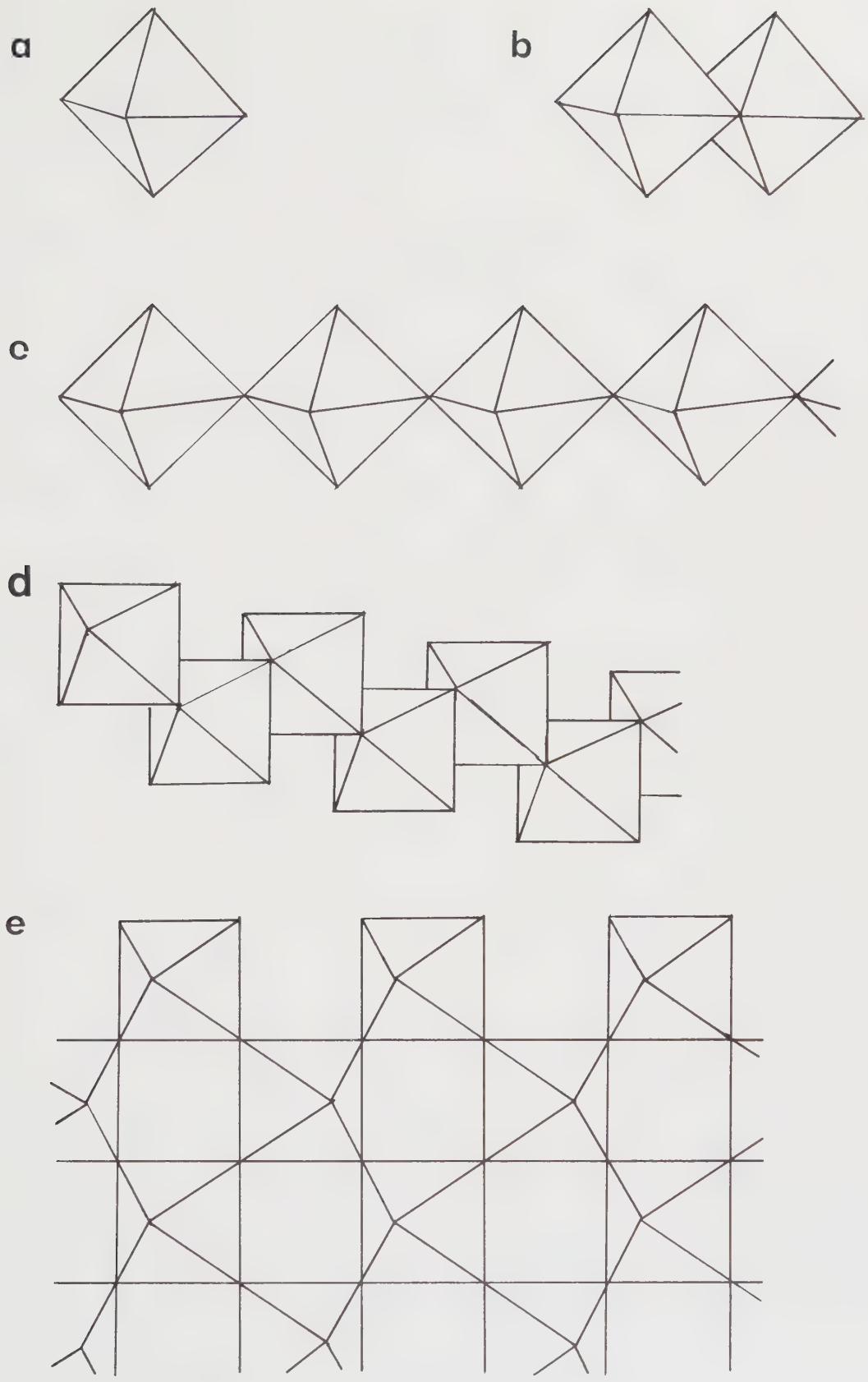


FIG 8. Schematic drawings of tellurate(VI) anions a) monomer, b) edge-sharing dimer, c) corner-sharing chain, d) edge-sharing chain, e) corner-sharing sheet. Lindqvist 1973

hydrate, $Te(OH)_6 \cdot 4H_2O$, and tri-copper tellurate(VI), Cu_3TeO_6. In the fourth, $CuTeO_4$, the Te(VI)-O octahedra are condensed to form infinite sheets as illustrated in Fig.8e.

A comparison of the $Te(OH)_6$ molecules found in cubic and monoclinic telluric acid and in the tetragonal hydrate indicate a slight elongation of the Te-O bonds in the latter structure (cf. Table 10). The neutron diffraction study indicates that the Te-O distance is 1.92-1.94 Å and, although the structure is not fully refined, there seems to be a significan elongation for two of the bonds in $Te(OH)_6 \cdot 4H_2O$. Lindqvist (1973) showed that all types of Te-O bond increases with the charge on the tellurate(VI) ion, i.e. Te-OH ~1.91 Å in $Te(OH)_6$, Te-OH ~1.93 Å in $TeO(OH)_5^-$ and Te-OH ~1.97 Å in $TeO_2(OH)_4^{2-}$. In the two latter anions the Te-O bond distances are 1.83 Å and 1.86 Å, respectively. In cubic and monoclinic telluric acid the $Te(OH)_6$ molecule cannot possibly achieve any extra negative charge. In $Te(OH)_6 \cdot 4H_2O$, on the other hand, the possibility of a net transfer between the H_2O and $Te(OH)_6$ molecules may be considered; i.e. transfer of negative charge from H_2O to $Te(OH)_6$. In other words there is a tendency for protons to be transferred from $Te(OH)_6$ to water, which is of course true, since the dissociation constant of telluric acid is $2.7\ 10^{-3}$ (Blanc, 1920). An average Te-OH distance of 1.926 Å in $Te(OH)_6 \cdot 4H_2O$ would thus correspond to an electron deficiency of ~ 0.1 per water molecule. A detailed description of the electron transfer in $Te(OH)_6 \cdot 4H_2O$ cannot be given until a precise model for the hydrogen bonds has been obtained. The distorted model in Table 7, with all hydrogen atoms distributed over 7 positions instead of 4 is probably a simplification. If it does not prove possible to solve the disorder problems adequately using the present data set, new X-ray and neutron diffraction data will be collected at low temperature (eg. -150°C).

There is also some evidence that the hydrogen positions in cubic $Te(OH)_6$ may be disordered, partly from a powder neutron diffraction investigation (Cohen- Addad, 1971) and partly since crystals of cubic $Te(OH)_6$ appear to transform to a tetragonal phase on ageing. It might therefore be profitable to investigate the structure of cubic $Te(OH)_6$ at + 100 °C, and it is also of great interest to study the structure of tetragonal $Te(OH)_6$. Detailed neutron diffraction investigations of the $Te(OH)_6$ molecule, hydrogen-bonded in four different phases, ought to supply new information about the general character of the hydrogen bond. Lindqvist and Lehman (1973) attributed the deviations of the O-Te-O angles from 90° in monoclinic $Te(OH)_6$ to hydrogen bonding. They found that the essential effect when a hydrogen bond is formed is that the electron density is increased in the accepting lone pair on the oxygen atom. Present knowledge concerning Te-O and O----O hydrogen bonds for the $Te(OH)_6$ molecule in different compounds is summarized in Table 10.

Cu_3TeO_6 also contains monomeric TeO_6 octahedra. It is a matter of definitio if the compound is to be regarded as a double oxide $3CuO \cdot TeO_3$ or as a salt containing Cu^{2+} and TeO_6^{6-} . However, the crystals are prepared from a solution of $CuSO_4$ and $Te(OH)_6$ in a hydrothermal reaction, which may be written $Te(OH)_6 + 3\ CuSO_4 \rightarrow Cu_3TeO_6 + 3H_2SO_4$. Under hydrothermal conditions one may thus regard telluric acid as stronger than sulfuric acid. One may also consider Cu_3TeO_6 as a copper(II) salt of telluric acid crystallized under hydrothermal conditions. However, Cu_3TeO_6 is insoluble in dilute and in conc. H_2SO_4 and the TeO_6^{6-} ion certainly does not exist in aqueous solution at NTP.

The geometrical dimensions of the TeO_6^{6-} ion fit well with the formula for π bond order ($\pi_{b.o.}$) in tellurates(VI) given by Lindqvist (1973): $\pi_{b.o.} = 6/(12 - 2n) - k_r \cdot n$, where n= tellurate charge and k_r= a repulsion

constant with an empirical value of 0.027. This formula gives $\pi_{b.o.}$=0.5 for the uncharged $Te(OH)_6$ molecule and $\pi_{b.o.}$=0.495 for the TeO_6^{6-} ion (n=6), corresponding to a Te-O bond length of ~ 1.91 Å.

Other similar structures are summarized in Table 11, and with the exceptio of Hg_3TeO_6, which has been determined to a relatively low accuracy, the bonds lengths fit very well with a π bond order of 0.5. According to Lindqvist (1973) the shortest observed Te-O bonds of 1.82 Å have $\pi_{b.o.}$= 0.8, while weaker bonds of 2.05 Å have $\pi_{b.o.}$=0.2. The $\sigma_{b.o.}$ is assumed to be 1.0 in all bonds.

The other copper(II) tellurate(VI) investigated, $CuTeO_4$, is prepared under approximately the same conditions as Cu_3TeO_6 (cf. page 3). Formally one may consider Cu_3TeO_6 as a salt of ortho-telluric acid, $Te(OH)_6$, while $CuTeO_4$ is a salt of meta-telluric acid, H_2TeO_4. This formulation is also structurally correct, since Cu_3TeO_6 contains monomeric TeO_6^{6-} ions and $CuTeO_4$ is built up from infinite two-dimensional sheets $[TeO_4]_n^{2n-}$ of the same kind as found in H_2TeO_4 (Moret,Philippot,Maurin and Lindqvist, 1974). The infinite ion $[TeO_4]_n^{2n-}$ may be of two kinds, namely edge-sharing chains (Fig. 8d) or corner-sharing sheets of TeO_6 octahedra (Fig. 8e). Structures containing these kinds of $[TeO_4]_n^{2n-}$ infinite anions are compared in Table 12.

In the case of $CuTeO_4$, the $[TeO_4]_n^{2n-}$ sheets are separated by Cu^{2+} ions. As discussed in Paper II there are two different ways of stacking the fully ordered layers, the Cu^{2+} ions in both cases having identical chemical environments. The two types of stacking occur in all crystals investigated, i.e. $CuTeO_4$ has an OD structure (Boll- Dornberger Schiff, 1966). When the connection points (in this case the Cu^{2+} ions) can have the symmetry $\bar{1}$,2 or m, the probability of OD stacking is high. In

Table 11. Bond distances and angles in some Me_3TeO_6 compounds.

	Te-O	Me-O	O-Te-O	ref.
Cu_3TeO_6	1.921(2)Å (6x)	1.949(2)-2.369(3) Å	94.0°(1)	Paper I
Mg_3TeO_6	1.912(3)Å-1.914(3)Å	2.022(4)-2.278(4)Å	94.6°(1)	Schulz and Bayer, 1970
Hg_3TeO_6	1.98*Å	2.33*	-	Falqui, 1963
Ba_2CuTeO_6	1.90(2)-1.93(2)Å	1.97(2)-2.25(2)Å	82.82-94.95	Köhl and Reinen, 1974
Be_4TeO_7	1.919(5)Å	1.614(2)-1.636(3)Å	-	Trömel, Maetz and Müllner, 1977

*No standard deviations given.

Table 12. Te-O distances in some tellurates(VI) of sheets and chains structure types.

a) corner-sharing sheet type

	$Te-O_{br}$	$Te-O_{term}$	ref.
Te_2O_5	1.907(5)-1.933(4)Å	1.848(4)-1.929(4)Å	Lindqvist, 1973
$H_2Te_2O_6$	1.940(5)-1.952(5)Å	1.864(5)-1.911(4)Å	Lindqvist and Moret, 1973
H_2TeO_4	1.905(8)-1.930(8)Å	1.903(8)Å	Moret, Philippot, Maurin, 1974
$CuTeO_4$	1.99(2)-2.02(2)Å	1.87(2)-1.91(1)Å	Paper II

b) edge-sharing chain type.

$KTeO_3(OH)$	1.994(2)-1.945(2)Å	1.843(3)Å	Lindqvist, 1972
Na_2TeO_4	1.97(2)-2.04(2)Å	1.85(2)Å	Kratochvíl and Jensovský, 1977
Li_2TeO_4	1.937(7)-2.044(11)Å	1.833(11)Å	Daniel, Moret, Philippot Maurin, 1977

$CuTeO_4$ the copper ions have a centrosymmetrical arrangement, which is quite natural for Cu^{2+}. In H_2TeO_4 on the other hand, the hydrogen atoms have, as expected, no symmetry, which makes an OD arrangement less probable and H_2TeO_4 is fully ordered. The two possible ways of stacking in $CuTeO_4$ each define a **structure of maximum degree of order, i.e.** MDO_1 and MDO_2. These are discussed in Paper II but are here further illustrated in Fig. 9 and Fig. 10. Fig.9 shows schematically the symmetry relations in the two MDO structures and Fig. 10 shows how three different reciprocal lattices occur, namely MDO_1, MDO_2 and MDO_2' (= mirror image of MDO_2). The presence of two or all three of the three structures results in streaks along b^* . The $\underline{h}\ 0\ \underline{l}$ reflections coincide, while on the even MDO_1 zones there will occur reflections also from the MDO_2 and MDO_2' structures at different positions due to which even zone is regarded. The MDO_2 and MDO_2' arrangements occur to a very low extent in $CuTeO_4$ (not detectable for most crystals investigated) (cf. Fig. 11).

The same type of disorder occurs for $PbTeO_4$, but in this case the monoclinic MDO_1 structure seems to be more unfavourable. (cf. Fig. 11) For the crystal investigated only the MDO_2 and MDO_2' structures could be detected. It should be noted that the rotation axis, b, coincides for the two structures. The details of the $PbTeO_4$ structure are not yet resolved, but this, together with other $MeTeO_4$ structures with possible disorder, ought to supply interesting information on how the Me^{2+} ions (= connection points between the ordered layers) influence the OD character. Vice versa, the OD character might provide additional information on the coordination chemistry of different Me^{2+} ions.
A compiled list of tellurium(VI)-oxygen bond distances is given in Table 1

$CuTeO_4$

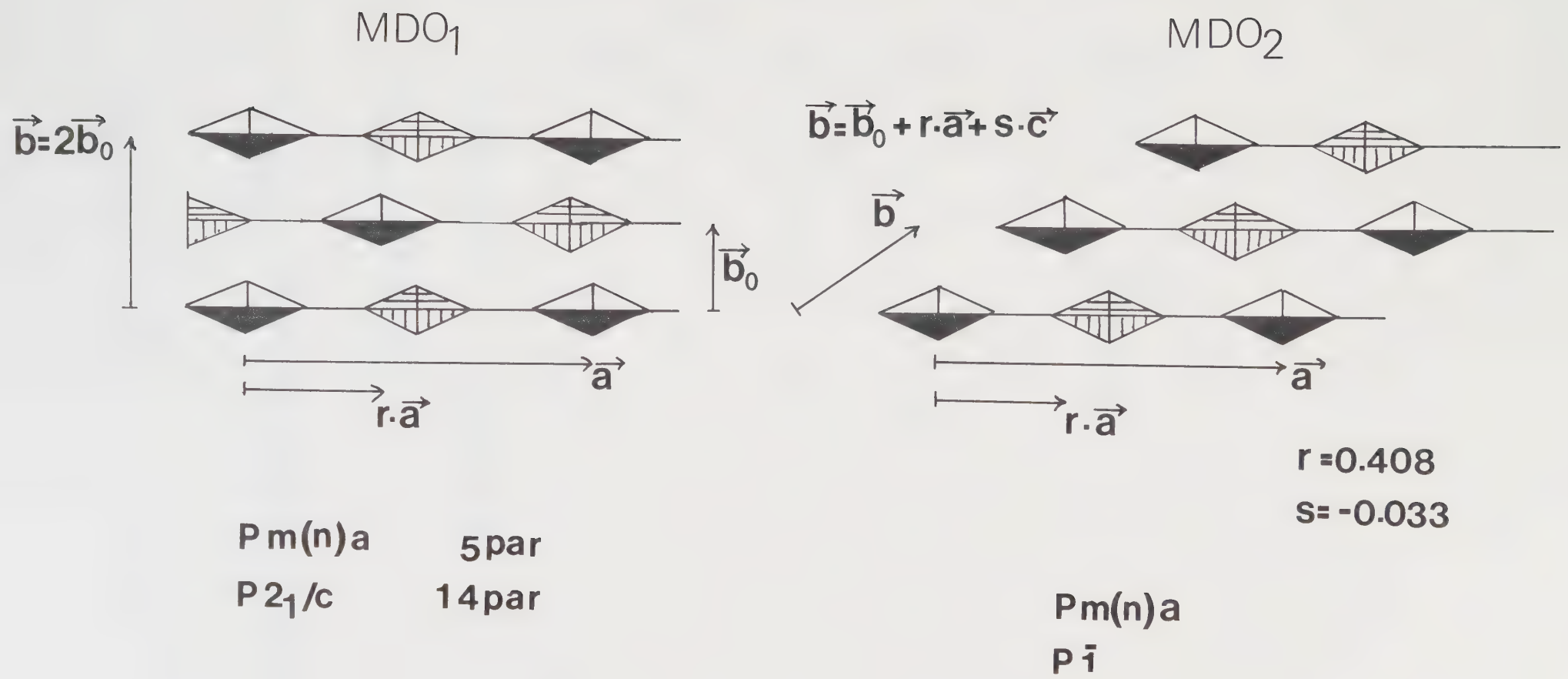
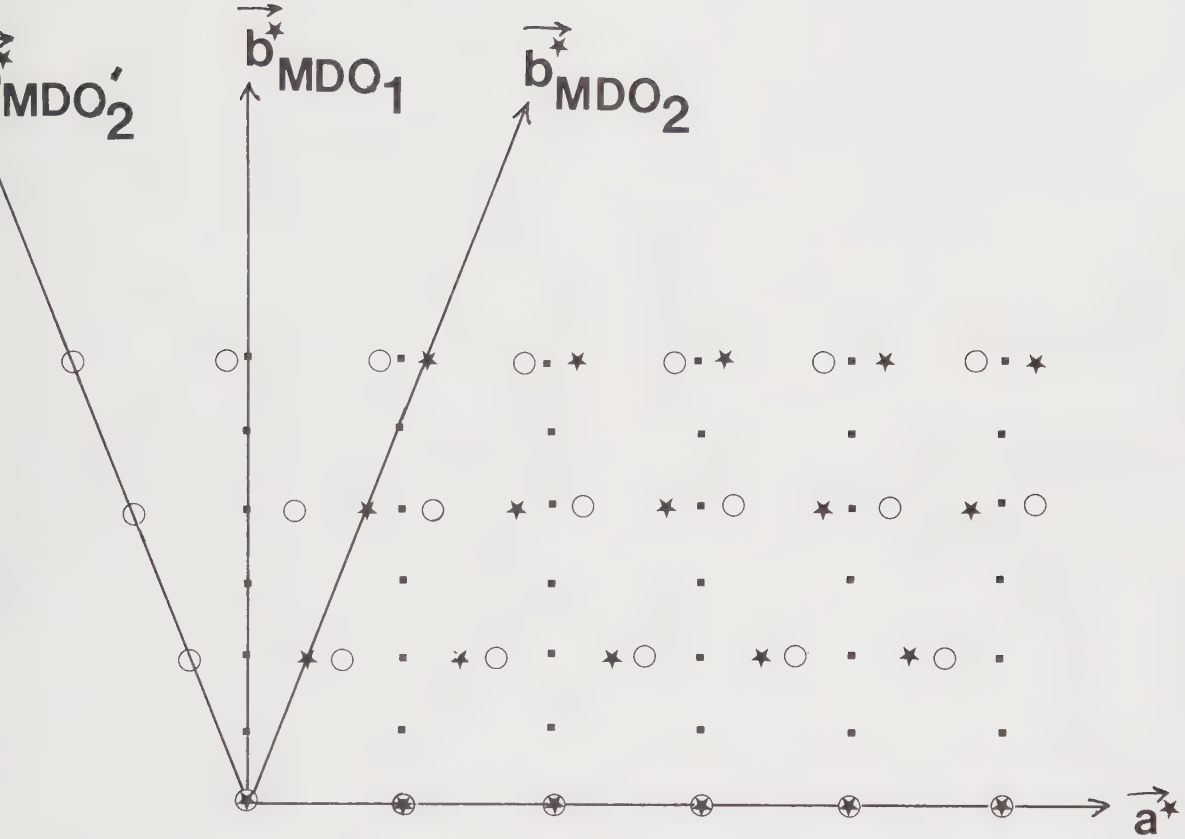


Fig. 9. The stacking of the layers (schematic illustration) in $CuTeO_4$

g. 4. The different reciprocal lattices of $CuTeO_4$.



$a = 5.50$ Å $c = 4.70$ Å

$b_{MDO_1} = 10.33$ Å

$b_{MDO_2} = \left[5.16^2 + (0.408 \cdot 5.5)^2 + (0.033 \cdot 4.7)^2\right]^{1/2} = 5.63$

$\gamma_{MDO_2} = 113.5^\circ$

Fig. 11 Weissenberg films of $PbTeO_4$ and $CuTeO_4$.

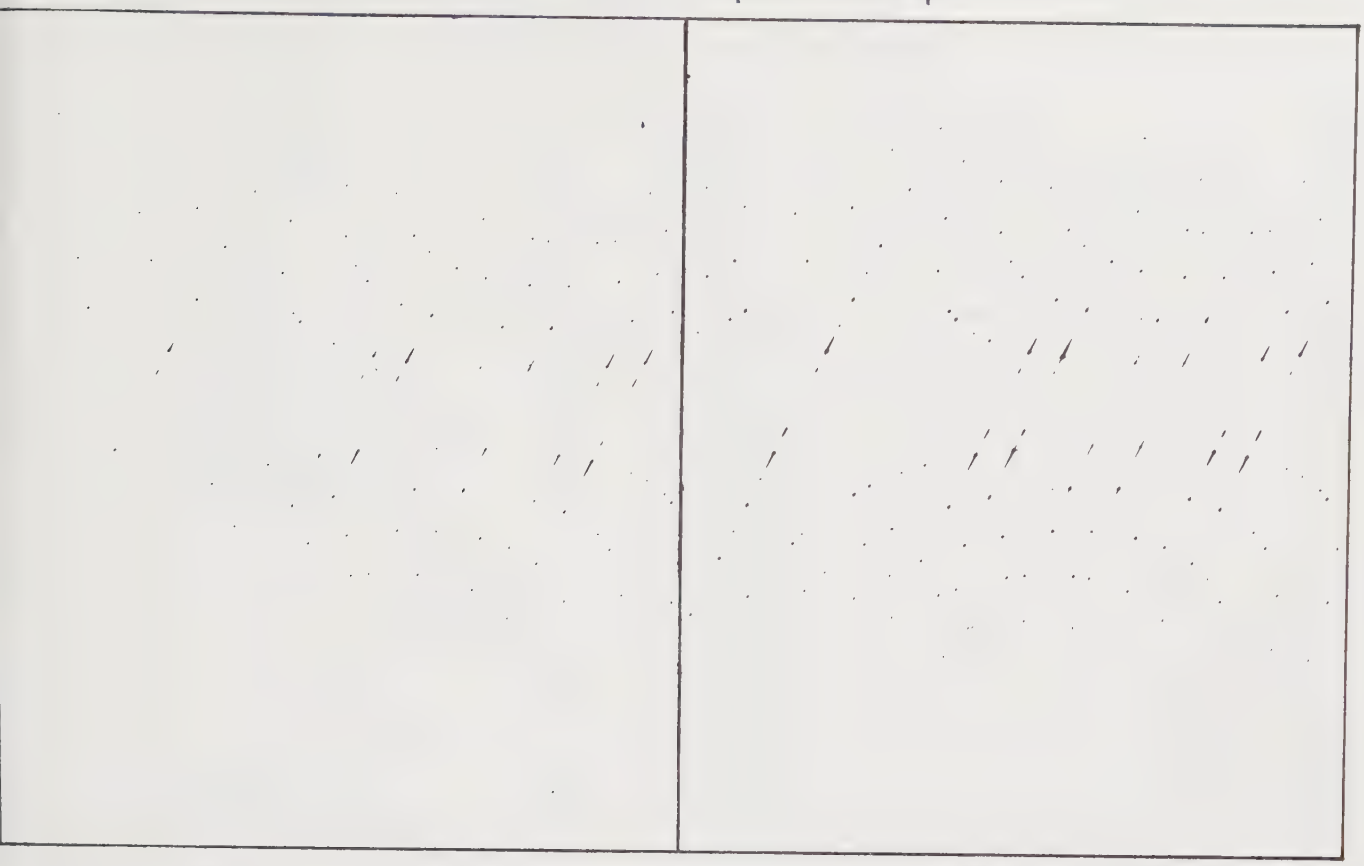


Fig.11a $PbTeO_4$ h 0 l Mo$K\alpha$, 45 h exposure crystal 1

Fig.11b $PbTeO_4$ h 0 l Mo$K\alpha$, 47 h exposure crystal 2

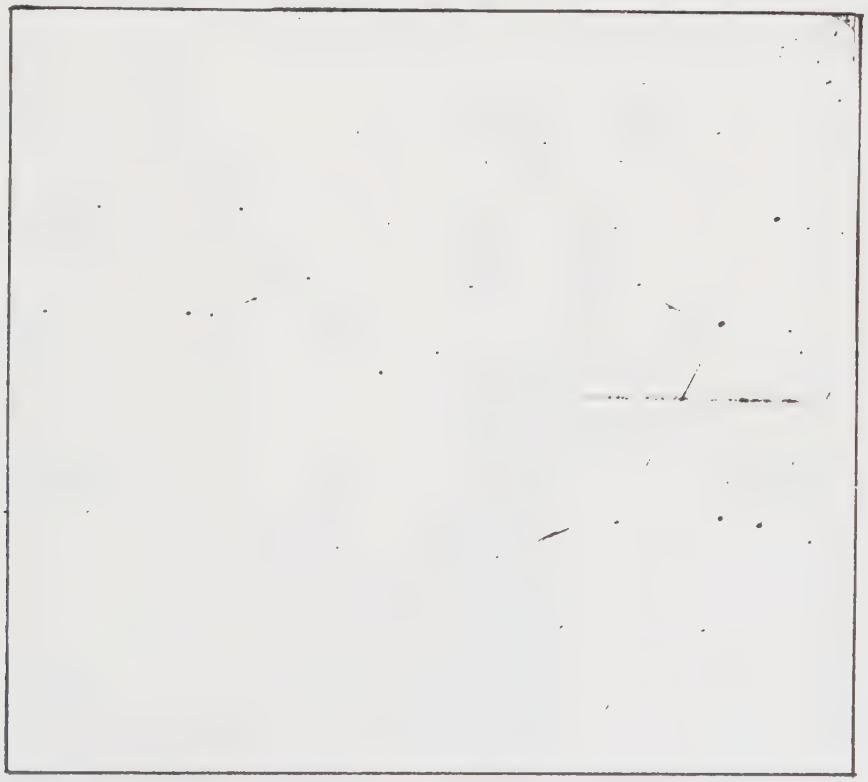


Fig.11c $CuTeO_4$, zero-layer rotated around [101], Cu$K\alpha$ 25 h exposure

Table 13. Tellurium(VI) - oxygen bond distances (Å).

	Compound	Ref.	Te-OH	Te-O	$Te\text{-}O_{Te(VI)}$	$Te\text{-}O_{Me}$
1.	$Te(OH)_6$(cub)	9	1.93			
2.	$Te(OH)_6$(cub)	34	1.88(3)			
3.	$Te(OH)_6$(cub)	III	1.913(6)			
4.	$Te(OH)_6$(mon)	25	1.905(5) 1.911(5) 1.916(5) 1.918(4) 1.918(5) 1.925(5)			
5.	$Te(OH)_6$(mon)	30	1.907(1) 1.908(1) 1.908(1) 1.908(1) 1.910(1) 1.914(1)			
6.	$Te(OH)_6 \cdot 4H_2O$		1.938(12) 2x 1.921(8) 4x			
7.	$Te(OH)_6NaF$	1	1.91(1) (3x) 1.92(1) (3x)			
8.	$Te(OH)_6 \cdot 2KF$	2	1.903(4) (2x) 1.911(4) (2x) 1.902(4) (2x)			
9.	$KTeO(OH)_5 \cdot H_2O$	37	1.90(2) 1.92(2) 1.92(2) 1.92(2) 1.94(2) 1.95(2)	1.83(2)		
10.	$KTeO_2(OH)_3$	22	1.89	1.89	1.84	

Table 13. Continued

	Compound	Ref.	Te-OH	Te-O	$Te-O_{Te(VI)}$	$Te-O_{Me}$
11.	$KTeO_3(OH)$	26	1.883(3)	1.843(3)	1.945(2) 1.947(2) 1.994(2) 1.997(2)	
12.	$Ag_2TeO_2(OH)_4$	16	1.95(8) 2.00(5)	1.85(9)		
13.	$K_4[Te_2O_6(OH)_4]\cdot 7.3H_2O$	28	1.99(1) 2.01(1)	1.86(1) 1.89(1)	1.99(1) 2.03(1)	
14.	$Na_{\frac{1}{2}}K_{3\frac{1}{2}}[Te_2O_6(OH)_4]\cdot 6H_2O$	27	1.97(4)	1.84(2) 1.87(2)	2.00(2) 2.03(2)	
15.	$H_2Te_2O_6$	30	1.904(5) 1.937(5)		1.940(5) 1.952(5)	1.864(5) 1.911(4)
16.	H_2TeO_4	35	1.903(8)		1.905(8) 1.930(8)	
17.	Te_2O_5	31			1.907(5) 1.927(5) 1.933(4) 1.927(4)	1.848(4) 1.929(4)
18.	$CuTeO_4$	II			1.87(2) 1.91(2)	1.91(1) 1.93(2) 1.99(2) 2.02(2)
19.	Li_2TeO_4	8		1.89	1.82 2.10	
20.	Li_2TeO_4	14			1.937(7)(2x) 1.833(11)(2x) 2.044(11)(2x)	
21.	Na_2TeO_4	19			1.85(2)(2x) 1.97(2)(2x) 2.04(2)(2x)	

Table 13. Continued

	Compound	Ref.	Te-OH	Te-O	$Te\text{-}O_{Te(VI)}$	$Te\text{-}O_{Me}$
22.	$Na_2K_4[Te_2O_8(OH)_2]\cdot 14H_2O$	24	2.03(2)	1.90(1) 1.91(1)	2.04(1)	
23.	Sr_2NiTeO_6	21				1.90(2) 1.91(1)
24.	Ba_2CuTeO_6	22				1.92(1)(2x
25.	Be_4TeO_7	41				1.93(1)(2x 1.92(2)(2x
26.	Mg_3TeO_6	38				1.912(3) 1.914(3)
27.	Hg_3TeO_6	15				1.98
28.	Cu_3TeO_6	10				1.91
29.	Cu_3TeO_6	I				1.921(2)
30.	$(NH_4)_2TeO_2(OH)_4$	17	1.958(1)(4x)	1.870(1)(2x)		

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REFERENCES

1. Allmann, R. (1976). Acta Cryst. B22 , 1025.
2. Allmann, R. and Haase,W. (1976). Inorg. Chem. Vol.15, No.4,1976.
3. Bayer, G. (1968). J. Less Common Metals. 16,215-222.
4. Berzelius, J.J. (1834). Pogg. Ann. 32
5. Berzelius, J.J. (1835). Ann. Chim. Phys. (2)58,43.
6. Blanc, E. (1920). J. Chim. Phys. 18,28-45.
7. Boll-Dornberger Schiff. (1966). Lehrgang über OD- Strukturen.
8. Cachau-Herreillat, D. Thesis Universite des Sciences et Techniques du Languedoc (1972) Montpellier, France.
9. Cohen-Addad,C. (1971). Bull. Soc. Fr. Mineral. Cristallogr. 94,172-174.
10. Coing-Boyat, J. and Hostachy,A.J.(1968). C.R. Acad. Sci. Sér.B, 267, 1435-1438.
11. Coppens, P.,Leiserowitz,L. and Rabinovich,D. (1965). Acta Cryst. 18, 1035-1038.
12. Coppens, P. and Hamilton,W.C. (1970). Acta Cryst. A26, 71-83.
13. Craven, B.M. and Sabine,T.M. (1966). Acta Cryst. 20, 214.
14. Daniel, F., Moret, J., Philippot, E. and Maurin, M. (1977). J. Solid State Chem. 22, 113-119.
15. Falqui, M.T. (1963). Rendicanti A, VOL.3, N.5, Serie 2.
16. Fischer, R. (1969). Monatsch. Chem. 100, 1809-1822.
17. Johansson, G.B. (1978). Acta Cryst. To be published.
18. Kirkpatrick, L.M. and Pauling,L. (1926). Z. anorg. Chem. 334, 225-234.
19. Kratochvíl,B. and Jensovsky´, L. (1977). Acta Cryst. B33, 2596-2598.
20. Köhl, P. and Reinen, D. (1974). Z. Anorg. Allg. Chem. 409, Heft 3, 257-352.
21. Köhl, P., Schultze-Rhonhof, E. and Malliao, W.J. (1971). Less Common Metals. 23, 313-315.

22. Lammers, P. and Zemann,J. (1965). Z. anorg. Chem.334, 225-234.

23. Lindgren, O. (1977). Thesis. University of Göteborg, Sweden.

24. Lindqvist, O. (1969). Acta Chem. Scand. 23, 3062-3070.

25. Lindqvist, O. (1970). Acta Chem. Scand. 24, 3178-3188.

26. Lindqvist, O. (1972). Acta Chem. Scand. 26, 4107-4120.

27. Lindqvist, O. (1973). Thesis. University of Göteborg, Sweden.

28. Lindqvist, O. and Lundgren, G. (1966). Acta Chem. Scand. 20, 2138-2155.

29. Lindqvist, O. and Wengelin, F. (1967). Ark. Kem. 28, 179-191.

30. Lindqvist, O. and Lehman, M.S. (1973). Acta Chem. Scand. 27, 85-95.

31. Lindqvist, O. and Moret, J. (1973). Acta Cryst. B29, 643.

32. Lindqvist, O. and Moret, J. (1973). Acta Cryst. B29, 956.

33. Lindqvist, O. and Ljungström, E. (1978). Acta Cryst. To be published.

34. Mahalaxmi, V. (1968). Thesis. Rensselear Polytechnic Institute. Troy, New York. (No 69-2487, Ann Arbor, Michigan).

35. Moret, J., Philippot, E., Maurin, M. and Lindqvist, O. (1974). Acta Cryst. B30, 1813-1818.

36. Mylius, F. (1901). Ber. 34, 2211,2214.

37. Raman, S. (1964). Inorg. Chem. 3, 634.

38. Schulz, H. and Bayer, G. (1971). Acta Cryst. B27, 815-821.

39. Sleight, A.W., Foris, C.M. and Licis, M.S. (1972). Inorg. Chem. Vol. 11, No.5, 1157-1158.

40. Stedman, R., Almqvist, L., Raunio, G. and Nilsson, G. (1969). Rev. Sci. Instrum. 40, 249-255.

41. Trömel, R., Martz, J. and Müllner, M. (1977). Acta Cryst. B33, 3959-396

42. Zachariasen, W. H. (1954). Acta Cryst. 7, 305.

Acta Cryst. (1978). B**34**, 896–897

Tricopper(II) Tellurate(VI)

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Abstract. Cu_3TeO_6, cubic, $Ia3$, $a = 9{\cdot}537$ (1) Å, $Z = 8$, $\rho_x = 6{\cdot}35$ g cm^{-3}. Refinement of the structure based on 330 independent reflections gave $R = 0{\cdot}022$. The structure is built up from TeO_6 octahedra connected through Cu atoms. The Te–O lengths are 1·921 (2) Å (6×), and the Cu–O coordination distances are 1·949 (2) (2×), 2·031 (3) (2×) and 2·369 (3) Å (2×).

Introduction. The structure of Cu_3TeO_6 has been determined from powder data by Hostachy & Coing-Boyat (1968). The Te^{VI} atoms were shown to be surrounded by six chemically equivalent O atoms, as in Mg_3TeO_6 (Schulz & Bayer, 1971) and $Te(OH)_6$ (Lindqvist & Lehmann, 1973). Such simple structures are of importance for a general discussion of octahedral Te^{VI}–O coordination.

Single crystals of Cu_3TeO_6 were prepared by hydrothermal synthesis. An aqueous solution of $CuSO_4$ (1 mol dm^{-3}) and $Te(OH)_6$ (0·5 mol dm^{-3}) was held at 700°C and 900 bar for one week, whereupon suitable crystals were deposited. The crystal selected for data collection was 0·13 × 0·10 × 0·13 mm and was mounted along **c** on a two-circle Pailred diffractometer. Graphite-monochromated Mo $K\alpha$ radiation was used, and intensities were measured with the ω-scan procedure and a scan speed of 2·5° min^{-1}. The background was measured for 24 s at each end of the scan interval. The layers $hk0$–$hk12$ ($k \geq 0$) were explored out to $2\theta \simeq 60°$, giving 1543 significant reflections with $\sigma(I)/I < 0{\cdot}3$.

The data were corrected for Lorentz and polarization (program *DATAP*1; O. Lindgren, Göteborg) and absorption effects (program *DATAP*2; Coppens, Leiserowitz & Rabinovich, 1965); $\mu_{MoK\alpha} = 218{\cdot}9$ cm^{-1}.

The space group $Ia3$ was confirmed by the systematic absences. Refinement was therefore commenced with the parameters given by Hostachy & Coing-Boyat (1968). A preliminary refinement with all 1543 observed reflections gave an R of 0·035. The parameters varied were atomic coordinates, anisotropic temperature factors and an isotropic extinction factor (program *LINUS*, Coppens & Hamilton, 1970). Before the final cycles, symmetry-related reflections were averaged giving 330 independent structure factors. Since each such structure factor was in general based on six ($n = 6$) independent measurements, it was considered profitable to use true statistical $\sigma(F)$ values according to $\sigma^2(F) = \Sigma_{i=1}^{n} (\bar{F} - F_i)^2/n(n-1)$. A final R of 0·026 ($R_w = 0{\cdot}023$) was thus obtained and the resulting structural parameters are given in Table 1.* Scattering factors given by Cromer & Waber (1965) were used for Te^0 and by Doyle & Turner (1968) for Cu^0 and O^0. Correction for the real part of the

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33149 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. *Atomic parameters*

The anisotropic temperature factor is $\exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2hka^*b^*U_{12} + 2hla^*c^*U_{13} + 2klb^*c^*U_{23})]$; the U_{ij} values are multiplied by 10^4.

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Te	$\frac{1}{8}$	$\frac{1}{4}$	$\frac{1}{4}$	35 (3)	35 (3)	35 (3)	4 (3)	4 (3)	4 (3)
Cu	0·96907 (6)	0	$\frac{1}{4}$	43 (2)	54 (2)	96 (2)	0	0	38 (2)
O	0·3675 (3)	0·1742 (3)	0·3950 (3)	7 (1)	64 (9)	43 (9)	18 (8)	23 (7)	16 (6)

anomalous scattering was applied for Te and Cu (Cromer, 1965).

The weight analysis (Table 2) shows some variation between the different F_o intervals. The effect is, however, reasonable, since there are few observations in each interval. The final refinement was also repeated with artificial weights according to Cruickshank's (1970) formula: $\sigma^2(F) = a + F_o + cF_o^2$, with $a = 100{\cdot}0$ and $c = 0{\cdot}002$. The weight analysis did not improve, although R dropped to 0·022. It is interesting to note that some rather small, but significant, differences occurred in both positional and thermal parameters, depending on which weighting procedure was used. The most obvious example is that the z coordinate of the O atom was 0·39502 (25) and 0·39679 (19) when absolute and artificial weights, respectively, were used.

Table 2. *Agreement analysis*

N is the number of reflections in each F_o interval and $w\Delta^2 = \Sigma_N w(F_o - |F_c|)^2$, where w corresponds to (*a*) statistical and (*b*) artificial weights.

F_o interval	N	(*a*) $w\Delta^2$	(*b*) $w\Delta^2$
0·0– 25·0	58	1·82	2·80
25·0– 28·2	41	1·21	1·28
28·2– 31·7	27	1·53	0·52
31·7– 36·5	29	0·51	0·30
36·5– 41·4	26	0·75	0·42
41·4– 49·9	23	0·99	0·75
49·9– 67·6	29	0·76	0·59
67·6– 86·0	33	0·52	0·42
86·0–111·3	34	1·01	0·51
111·3–355·0	30	0·49	0·56

	(*a*)	(*b*)
$\sigma^2(F_o)$	$\Sigma_{i=1}^{n}(\bar{F}_o - F_{o,i})^2/n(n-1)$	$100{\cdot}0 + F_o + 0{\cdot}002F_o^2$
$R = \Sigma\|\|F_o - \|F_c\|\|/\Sigma F_o$	0·026	0·022
$R_w = (\Sigma w\|F_o - \|F_c\|^2/\Sigma wF_o^2)^{1/2}$	0·023	0·031

Table 3. *Interatomic distances* (Å) *and angles* (°) *in* Cu_3TeO_6

Te–O	(6×)	1·921 (2)	O(i)–Cu–O′(ii)	166·3 (1)
Cu–O(i)	(2×)	1·949 (2)	O(i)–Cu–O(iii)	91·9 (1)
Cu–O(ii)	(2×)	2·031 (2)	O(i)–Cu–O′(iii)	120·6 (1)
Cu–O(iii)	(2×)	2·369 (3)	O(ii)–Cu–O′(ii)	95·5 (2)
O–Te–O	(6×)	94·0 (1)	O(ii)–Cu–O(iii)	75·4 (1)
O–Te–O	(6×)	86·0 (1)	O(ii)–Cu–O′(iii)	72·6 (1)
O(i)–Cu–O′(i)		96·6 (1)	O(iii)–Cu–O′(iii)	131·7 (1)
O(i)–Cu–O(ii)		85·6 (1)		

Discussion. Interatomic distances and angles are given in Table 3. The O atoms are approximately cubic close packed. The average volume per O atom is 18·1 Å^3, while the value for ideal close packing is 15·6 Å^3 (Pauling, 1960). This difference is due to the action of the Te and Cu coordination polyhedra.

The Cu atoms are surrounded by a distorted octahedral arrangement of O atoms (Table 3). The O atoms involved in the four strongest bonds are each shifted 0·2 Å from a planar configuration. The Cu–O interactions may thus be considered as mainly ionic, compared with the octahedral Te–O bonds, and the structure may be considered as being built up from Cu^{2+} and TeO_6^{6-} ions.

The Te atom is situated on a threefold inversion axis, *i.e.* the Te bonding orbital system has C_{3i} symmetry. The same symmetry has also been found in Mg_3TeO_6 (Schulz & Bayer, 1971), and the dimensions of the TeO_6^{6-} ion found in this structure are, within experimental error, the same as in Cu_3TeO_6. In Mg_3TeO_6 the Te–O bond is 1·913 (3) Å, and the O–Te–O angle generated by the threefold rotation is 94·2 (1)°, corresponding to 1·921 (2) Å and 94·0 (1)° in Cu_3TeO_6. It thus seems that the TeO_6 unit when occurring as a TeO_6^{6-} ion is rigid and has a definite bond distance of 1·91–1·92 Å. In $Te(OH)_6$ the mean Te–O bond distance was 1·910 (1) Å (Lindqvist & Lehmann, 1973).

The TeO_6^{6-} ion may occur in melts and in aqueous solutions under high pressure and temperatures.

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References

Coppens, P. & Hamilton, W. C. (1970). *Acta Cryst.* A**26**, 71–83.

Coppens, P., Leiserowitz, L. & Rabinovich, D. (1965). *Acta Cryst.* **18**, 1035–1038.

Cromer, D. T. (1965). *Acta Cryst.* **18**, 17–23.

Cromer, D. T. & Waber, J. T. (1965). *Acta Cryst.* **18**, 104–109.

Cruickshank, D. W. J. (1970). *Crystallographic Computing*, p. 195. Copenhagen: Munksgaard.

Doyle, P. A. & Turner, P. S. (1968). *Acta Cryst.* A**24**, 390–399.

Hostachy, A. & Coing-Boyat, J. (1968). *C. R. Acad. Sci. Sér. B*, **267**, 1435–1438.

Lindqvist, O. & Lehmann, M. S. (1973). *Acta Chem. Scand.* **27**, 85–95.

Pauling, L. (1960). *The Nature of the Chemical Bond*, 3rd ed. Ithaca: Cornell Univ. Press.

Schulz, H. & Bayer, G. (1971). *Acta Cryst.* B**27**, 815–821.

h	k	l	F_{hkl}	$F_{\bar{h}kl}$	$F_{\bar{l}hk}$	$F_{\bar{l}\bar{h}k}$	F_{klh}	$F_{\bar{k}lh}$	$\bar{F}_o$	F_c	$\sigma(F)$
0	0	2	109.7	111.1	112.0	0.0	0.0	0.0	110.9	111.4	0.7
0	0	4	278.8	269.4	269.5	0.0	0.0	0.0	272.6	318.6	3.1
0	0	6	89.1	89.9	85.9	0.0	0.0	0.0	88.3	89.2	1.2
0	0	8	250.2	234.4	231.1	0.0	0.0	0.0	238.6	247.2	5.9
0	0	10	107.0	103.5	97.6	0.0	0.0	0.0	102.7	103.0	2.7
0	0	12	126.8	123.1	102.3	0.0	0.0	0.0	123.4	127.9	1.9
0	0	14	108.4	105.5	105.6	0.0	0.0	0.0	106.5	108.6	0.9
0	0	16	85.8	79.7	0.0	0.0	0.0	0.0	82.7	82.6	3.1
0	2	2	71.2	0.0	71.5	0.0	66.0	70.1	69.7	69.4	1.3
0	2	4	47.9	0.0	0.0	0.0	40.6	38.9	42.5	38.5	2.8
0	2	6	109.7	113.0	111.9	0.0	0.0	114.4	112.2	114.3	1.0
0	2	10	99.8	101.5	88.4	0.0	0.0	103.3	100.7	103.0	1.1
0	2	14	107.1	108.7	0.0	0.0	0.0	0.0	107.9	112.0	0.8
0	4	4	325.8	335.1	312.7	0.0	0.0	332.8	326.6	375.0	5.0
0	4	6	130.9	137.1	133.5	0.0	0.0	137.5	134.7	136.7	1.6
0	4	8	186.7	186.8	189.6	0.0	0.0	195.5	189.6	194.7	2.1
0	4	10	114.6	114.7	113.2	0.0	0.0	110.7	113.3	114.3	0.9
0	4	12	104.0	104.7	109.3	0.0	0.0	109.8	106.9	109.6	1.5
0	4	14	90.1	90.3	0.0	0.0	0.0	90.9	90.4	93.2	0.2
0	4	16	0.0	0.0	58.5	0.0	0.0	0.0	58.5	64.9	7.7
0	6	6	46.9	0.0	44.4	0.0	0.0	44.9	45.4	43.6	0.8
0	6	8	41.1	41.6	43.5	0.0	0.0	43.4	42.4	40.8	0.6
0	6	10	94.2	94.6	94.3	0.0	0.0	97.8	95.2	96.1	0.9
0	6	14	63.0	57.1	0.0	0.0	0.0	0.0	60.1	63.0	3.0
0	8	8	115.8	120.6	116.5	0.0	0.0	124.3	119.3	119.9	2.0
0	8	10	130.2	132.5	129.1	0.0	0.0	132.3	131.0	133.0	0.8
0	8	12	81.4	78.9	77.2	0.0	0.0	78.6	79.1	78.3	0.9
0	8	14	104.4	100.5	0.0	0.0	0.0	0.0	102.4	103.6	1.9
0	10	10	32.7	36.3	35.2	0.0	0.0	38.1	35.5	36.3	1.1
0	10	12	46.9	45.0	41.8	0.0	0.0	46.0	44.9	43.8	1.1
0	12	12	44.3	0.0	38.2	0.0	0.0	0.0	41.3	42.4	3.0
1	1	2	43.2	50.9	53.0	48.7	49.1	52.0	49.3	49.3	1.2
1	1	4	25.8	25.9	27.9	22.1	24.9	26.9	25.7	26.1	0.7
1	1	6	72.1	76.3	78.9	78.3	77.3	80.1	77.1	77.6	1.1
1	1	8	72.5	78.6	80.3	82.3	72.1	81.1	78.1	82.3	1.6
1	1	10	34.0	37.9	42.3	42.0	40.0	38.9	38.5	38.2	1.2
1	1	12	15.1	25.3	0.0	25.1	24.2	22.6	21.1	23.9	2.0
1	2	3	27.2	27.8	29.2	29.5	28.5	29.7	28.7	28.9	0.4
1	2	5	34.4	40.7	42.4	0.0	37.2	41.4	39.2	38.5	1.5
1	2	9	0.0	16.2	0.0	0.0	0.0	0.0	16.2	15.5	4.0
1	2	11	36.3	37.4	44.0	43.1	39.5	36.0	39.4	39.7	1.4
1	3	4	69.5	72.5	75.4	71.5	70.5	74.2	72.3	73.4	0.9
1	3	6	72.5	73.1	75.2	72.6	72.1	71.6	72.8	73.9	0.5
1	3	8	46.6	48.7	46.9	46.0	49.2	47.5	47.5	48.2	0.5
1	3	10	44.0	46.3	49.5	43.7	43.4	45.2	45.4	45.9	0.9
1	3	12	24.8	23.4	26.8	28.6	21.5	22.0	24.5	24.6	1.1
1	4	5	72.6	74.8	74.8	73.4	72.1	74.0	73.6	74.3	0.5
1	4	7	33.1	34.7	37.1	35.1	35.1	36.5	35.3	34.7	0.6
1	4	9	24.5	24.5	23.5	22.7	26.0	22.7	24.0	23.9	0.5
1	4	11	23.7	24.1	20.5	26.8	24.1	24.8	24.0	25.9	0.8
1	4	13	0.0	0.0	29.5	25.6	27.6	26.7	27.3	27.5	0.8
1	4	15	0.0	0.0	0.0	23.1	21.9	0.0	22.5	21.7	0.6
1	5	6	41.7	42.7	43.3	41.9	42.6	42.4	42.4	43.5	0.2
1	5	8	39.7	39.1	42.4	42.6	40.9	42.6	41.2	39.4	0.6
1	5	10	46.9	44.3	44.5	44.9	44.3	47.3	45.4	47.2	0.6
1	5	12	29.8	26.6	27.7	26.1	27.5	27.6	27.9	30.3	0.6

1	6	7	52.3	53.4	53.5	55.9	53.7	55.0	54.0	55.0	0.5
1	6	9	52.2	52.9	55.9	54.8	54.1	54.7	54.1	54.5	0.5
1	6	11	22.6	26.9	21.6	20.8	22.4	23.6	23.0	22.0	0.9
1	6	13	0.0	0.0	0.0	0.0	26.4	30.3	28.4	27.0	2.0
1	6	15	0.0	0.0	28.6	28.7	0.0	32.0	29.8	30.5	1.1
1	7	8	35.0	39.0	35.3	35.2	35.4	33.8	35.6	36.5	0.7
1	7	10	39.5	44.3	38.7	38.3	41.2	32.6	39.1	39.8	1.6
1	7	12	23.2	24.7	23.8	25.8	27.5	27.5	25.4	25.7	0.8
1	8	9	42.7	45.4	48.1	44.0	44.7	43.9	44.8	45.0	0.8
1	8	11	28.6	29.5	0.0	30.4	29.8	23.5	28.4	29.0	1.3
1	8	13	0.0	0.0	0.0	27.1	31.9	27.2	28.7	25.5	1.6
1	9	12	31.6	35.1	30.3	31.6	30.6	33.8	32.2	31.9	0.8
1	10	11	32.2	0.0	30.4	28.8	28.9	0.0	30.1	28.2	0.8
1	10	13	0.0	0.0	28.7	32.0	0.0	0.0	30.3	28.9	1.6
1	11	12	0.0	0.0	0.0	10.6	0.0	0.0	10.6	10.4	3.3
2	0	4	0.0	78.1	77.0	75.9	76.6	0.0	76.9	76.4	0.5
2	0	6	0.0	31.6	31.3	30.6	30.8	0.0	31.1	30.4	0.2
2	0	8	0.0	130.7	133.8	134.1	131.8	0.0	132.6	135.3	0.8
2	0	12	0.0	103.3	104.6	109.8	104.3	0.0	105.4	107.7	1.4
2	0	14	0.0	0.0	0.0	0.0	22.8	0.0	22.8	18.7	4.8
2	0	16	0.0	0.0	93.5	99.0	0.0	0.0	96.4	98.4	2.6
2	1	5	21.3	25.6	27.0	0.0	23.1	27.3	24.9	23.8	1.2
2	1	7	54.7	57.9	56.7	57.5	56.5	57.1	56.7	56.3	0.5
2	1	9	26.5	26.7	27.1	27.5	29.2	28.1	27.5	29.1	0.4
2	2	2	337.0	0.0	0.0	335.0	0.0	0.0	336.0	434.8	1.0
2	2	4	88.1	94.7	97.2	91.1	0.0	95.4	92.6	92.1	1.5
2	2	6	256.8	260.9	276.6	265.6	265.2	270.9	266.0	291.5	2.9
2	2	8	100.6	104.9	104.7	103.1	105.2	106.3	102.8	104.7	1.5
2	2	10	144.5	0.0	155.5	152.5	151.1	151.6	151.0	156.6	1.8
2	2	12	99.6	104.3	104.0	101.3	102.2	103.4	101.1	104.2	1.5
2	2	14	0.0	0.0	88.9	89.2	90.9	88.8	89.4	93.2	0.5
2	2	16	0.0	0.0	78.9	77.3	0.0	0.0	78.1	81.5	0.8
2	3	3	77.1	82.9	84.3	77.9	77.1	84.6	80.4	79.2	1.3
2	3	5	19.7	21.0	21.9	0.0	0.0	22.6	21.3	20.2	0.6
2	3	7	18.1	17.4	0.0	0.0	0.0	0.0	17.8	16.6	0.4
2	3	11	28.9	30.8	30.0	29.7	27.9	30.1	29.5	30.9	0.4
2	4	4	78.0	81.8	85.6	79.8	78.4	91.0	82.1	81.9	1.8
2	4	6	40.1	42.2	39.6	40.6	42.0	40.7	40.9	39.5	0.4
2	4	8	80.3	87.2	89.6	86.1	72.7	85.4	83.5	83.3	2.5
2	4	12	102.6	108.5	106.2	106.9	106.1	105.6	106.0	106.9	0.8
2	5	5	29.1	32.2	34.6	32.1	28.0	34.3	31.4	31.1	1.0
2	5	7	17.2	0.0	0.0	0.0	0.0	0.0	17.2	17.3	4.1
2	5	13	0.0	0.0	26.7	31.4	30.4	30.1	29.7	29.3	1.0
2	6	6	185.0	187.0	193.6	188.2	187.7	196.0	189.1	197.1	1.5
2	6	8	119.1	123.9	121.7	117.4	118.1	122.0	120.4	121.6	1.0
2	6	10	118.8	122.4	120.9	118.4	0.0	121.4	120.4	123.1	0.8
2	6	12	103.2	107.7	104.9	0.0	106.6	110.1	106.5	106.2	1.2
2	6	14	0.0	0.0	67.5	66.2	67.6	68.7	67.5	68.3	0.5
2	7	7	34.0	36.8	38.3	32.8	30.5	32.0	33.2	33.9	1.3
2	7	9	0.0	0.0	0.0	0.0	12.0	0.0	12.0	14.9	3.5
2	8	8	55.6	56.0	60.9	57.3	57.9	57.3	57.1	56.5	0.8
2	8	10	37.9	37.1	35.7	34.3	27.9	35.0	34.6	36.7	1.5
2	8	12	60.9	60.6	55.6	57.6	62.9	61.4	59.8	60.3	1.1
2	9	9	28.3	25.2	25.2	27.9	28.8	27.6	27.2	27.9	0.7
2	9	11	0.0	0.0	0.0	20.3	0.0	0.0	20.3	13.3	4.5
2	10	10	69.6	70.6	73.5	70.4	70.1	68.6	70.7	71.0	0.6

2	10	12	114.0	113.3	113.8	112.6	114.5	113.2	113.6	114.8	0.3
3	1	4	83.7	87.6	87.0	82.6	83.2	85.3	84.9	85.0	0.8
3	1	6	61.8	65.8	63.5	61.2	63.0	62.3	62.9	63.8	0.7
3	1	8	37.1	39.6	36.3	36.6	34.9	37.5	37.0	37.6	0.6
3	1	10	39.6	41.1	37.6	40.2	43.2	38.9	40.1	41.1	0.8
3	1	12	37.3	38.6	38.1	39.8	38.1	35.9	37.6	39.6	0.6
3	2	5	24.4	26.5	26.8	26.3	23.5	24.8	25.4	25.3	0.6
3	2	7	17.8	18.9	0.0	23.2	0.0	0.0	20.0	19.1	1.6
3	2	9	20.4	22.0	27.7	22.1	22.8	0.0	23.0	23.2	1.2
3	2	15	0.0	0.0	0.0	22.5	0.0	21.4	21.9	19.8	0.6
3	3	4	39.4	42.8	43.6	42.0	40.5	45.5	42.0	43.0	0.8
3	3	6	40.4	42.0	42.7	37.9	39.6	38.8	40.2	41.2	0.8
3	3	8	59.9	62.9	62.3	58.5	61.5	61.0	60.7	60.9	0.6
3	3	10	52.9	52.6	54.2	48.6	51.2	51.2	51.5	52.8	0.7
3	3	12	24.0	22.5	0.0	0.0	23.8	23.2	23.4	23.2	0.3
3	4	5	37.8	36.4	34.6	33.8	34.3	36.7	35.3	35.5	0.5
3	4	7	37.0	38.2	40.0	35.2	37.3	36.6	37.4	38.3	0.7
3	4	9	33.9	38.6	31.8	34.4	36.9	35.8	35.2	36.4	1.0
3	4	11	32.4	36.7	29.3	35.9	36.5	36.8	34.6	35.6	1.3
3	5	6	54.2	58.0	57.0	54.6	53.5	60.3	56.2	57.0	1.1
3	5	8	60.8	62.6	62.7	60.6	59.1	63.5	61.5	61.1	0.7
3	5	10	28.5	33.4	31.7	32.9	30.3	29.1	31.0	30.4	0.8
3	5	12	18.9	0.0	0.0	22.0	24.0	22.4	21.8	20.4	1.1
3	6	7	50.5	50.1	53.8	53.0	49.6	53.2	51.7	52.0	0.7
3	6	9	21.9	25.7	22.7	25.4	23.9	25.8	24.2	24.6	0.7
3	6	11	35.6	40.5	0.0	38.2	40.2	36.5	38.2	39.7	1.0
3	6	13	0.0	0.0	28.9	0.0	24.1	29.5	27.5	24.8	1.7
3	7	8	40.0	42.6	45.1	42.7	41.3	41.2	42.2	43.8	0.7
3	7	10	26.1	29.8	26.1	25.0	26.3	27.6	26.8	27.1	0.7
3	7	12	0.0	0.0	0.0	0.0	20.9	0.0	20.9	17.5	4.6
3	8	9	34.2	38.1	33.7	37.0	37.3	39.2	36.5	36.4	0.9
3	8	11	23.0	25.2	28.1	30.1	26.2	28.6	26.9	27.3	1.1
3	8	13	0.0	0.0	28.3	30.0	28.2	23.8	27.6	27.9	1.3
3	9	10	32.1	30.9	31.6	28.6	29.5	26.4	29.9	30.8	0.9
3	10	11	28.3	0.0	24.5	24.6	0.0	26.9	26.1	25.3	0.9
3	10	13	0.0	0.0	0.0	23.7	0.0	0.0	23.7	18.9	4.9
4	0	6	0.0	86.8	85.9	81.1	0.0	81.5	83.8	82.7	1.5
4	0	8	0.0	186.3	188.5	189.6	0.0	186.1	187.6	196.6	0.8
4	0	10	0.0	106.1	104.5	103.0	0.0	102.5	104.0	104.3	0.8
4	0	12	0.0	103.8	102.1	106.8	0.0	108.2	105.2	105.1	1.4
4	0	14	0.0	0.0	70.3	71.5	0.0	67.8	69.9	70.2	1.1
4	0	16	0.0	0.0	0.0	0.0	72.1	0.0	72.1	73.1	8.5
4	1	5	78.0	80.6	74.4	70.6	75.0	75.8	75.7	76.1	1.4
4	1	7	35.8	38.4	35.5	35.8	37.1	31.7	35.7	36.1	0.9
4	1	9	27.5	29.5	26.2	29.4	24.0	24.6	26.9	26.0	1.0
4	1	11	20.2	27.1	20.5	22.1	23.8	0.0	22.6	23.2	1.0
4	1	13	0.0	0.0	0.0	29.8	23.4	27.2	26.8	25.2	1.8
4	2	6	101.3	105.0	105.5	100.8	99.1	101.8	102.2	100.6	1.0
4	2	8	23.7	27.5	0.0	0.0	20.6	0.0	23.9	19.4	2.0
4	2	10	119.7	131.5	127.5	121.6	122.4	124.6	124.6	125.1	1.8
4	2	14	0.0	0.0	97.3	96.9	96.1	97.6	97.0	98.3	0.3
4	3	5	29.8	33.3	36.9	30.7	28.9	30.3	31.7	31.9	1.2
4	3	7	33.1	38.0	34.7	36.5	29.2	34.1	34.3	35.9	1.2
4	3	9	30.9	33.7	36.2	30.0	31.6	31.0	32.2	32.0	0.9
4	3	11	23.7	20.2	22.1	0.0	0.0	22.4	22.1	22.1	0.7
4	3	13	0.0	0.0	0.0	0.0	26.5	23.6	25.1	23.0	1.4

4	4	4	231.5	0.0	0.0	227.5	0.0	245.3	234.8	252.2	5.4
4	4	6	75.0	78.1	78.2	76.5	78.5	82.8	78.2	75.8	1.1
4	4	8	156.3	167.9	166.3	158.8	158.2	164.0	161.1	164.3	1.9
4	4	10	95.7	98.2	99.8	94.7	98.3	99.4	97.3	97.0	0.8
4	4	12	98.0	103.4	100.5	95.5	99.7	103.0	99.4	101.7	1.2
4	4	14	0.0	0.0	95.8	95.6	97.6	96.1	96.3	97.7	0.5
4	5	5	23.9	23.3	21.7	24.2	28.5	32.1	25.8	22.7	1.4
4	5	7	31.6	31.8	31.8	28.5	27.9	35.0	31.1	32.2	1.1
4	5	9	41.5	43.8	43.3	40.3	40.8	42.3	42.0	42.1	0.6
4	5	11	0.0	0.0	22.2	0.0	0.0	22.8	22.5	20.0	0.3
4	6	6	75.1	77.9	80.8	75.0	75.3	77.7	76.8	76.4	0.8
4	6	8	46.4	48.0	46.4	44.4	45.1	46.7	46.2	45.7	0.5
4	6	10	70.4	71.6	0.0	71.0	75.1	72.6	72.2	71.7	0.8
4	6	12	22.7	24.4	24.4	0.0	25.3	24.5	24.3	22.6	0.4
4	6	14	0.0	0.0	91.9	90.1	89.8	92.8	91.2	94.3	0.7
4	7	7	37.7	39.6	38.4	38.1	42.1	37.9	38.9	38.0	0.6
4	7	9	23.6	31.0	31.4	27.1	26.6	26.9	27.8	28.8	1.2
4	7	11	21.1	23.6	0.0	0.0	23.9	0.0	22.9	19.0	0.9
4	8	8	116.5	120.7	121.9	116.7	117.8	120.9	118.7	121.2	0.9
4	8	10	93.9	97.5	97.5	95.6	98.8	99.9	97.2	97.6	0.9
4	8	12	60.1	61.4	63.0	59.8	59.1	63.5	61.1	61.6	0.7
4	9	13	0.0	0.0	26.9	22.3	0.0	24.5	24.6	23.5	1.3
4	10	10	50.7	49.8	52.7	50.7	50.2	46.0	50.5	49.3	0.9
4	10	12	32.4	35.1	0.0	29.8	37.4	31.4	33.2	32.4	1.3
4	11	11	0.0	0.0	27.0	0.0	23.0	0.0	25.0	22.4	2.0
4	12	12	44.7	48.9	40.3	43.6	0.0	0.0	44.4	44.4	1.8
5	1	6	37.1	41.5	34.8	35.2	41.0	37.4	37.8	37.1	1.2
5	1	8	41.7	39.8	39.9	40.5	42.4	42.0	41.1	41.1	0.5
5	1	10	56.7	61.9	57.7	56.6	55.3	52.6	56.8	57.3	1.2
5	1	12	28.3	26.7	27.3	22.8	25.9	24.9	26.0	25.5	0.8
5	2	7	32.6	31.8	32.3	0.0	34.1	28.7	31.9	33.2	0.9
5	2	15	0.0	24.3	0.0	0.0	0.0	0.0	24.3	22.8	4.9
5	3	6	66.4	70.2	69.3	63.3	64.8	65.7	66.6	67.6	1.1
5	3	8	46.5	48.5	46.0	45.8	47.9	44.7	46.6	47.5	0.6
5	3	10	21.7	25.5	23.0	21.0	26.6	24.1	23.7	23.1	0.9
5	3	12	30.8	34.2	31.8	32.5	29.6	29.7	31.4	31.5	0.7
5	3	14	0.0	0.0	23.4	0.0	0.0	0.0	23.4	18.5	4.8
5	4	7	38.3	39.2	35.6	34.3	32.8	35.6	36.0	37.2	1.0
5	4	9	43.2	41.7	40.0	40.4	40.2	40.5	41.0	42.4	0.5
5	4	11	21.2	28.4	0.0	21.1	27.7	29.0	25.5	24.9	1.8
5	4	13	0.0	0.0	0.0	0.0	0.0	21.3	21.3	16.7	4.6
5	5	6	58.4	59.3	57.7	56.9	55.4	58.6	57.7	57.8	0.6
5	5	8	58.3	61.5	59.4	60.0	59.3	57.5	59.3	59.9	0.5
5	5	10	25.8	29.3	24.5	0.0	23.0	23.6	25.2	23.6	1.1
5	5	12	26.3	28.2	28.9	27.9	29.4	25.5	27.5	27.6	0.6
5	6	7	32.2	35.5	32.4	30.7	34.0	29.9	32.4	33.2	0.8
5	6	9	32.1	28.8	0.0	28.4	29.8	28.7	29.5	31.7	0.7
5	6	11	34.6	30.0	29.0	29.6	32.6	31.1	31.1	32.7	0.9
5	6	13	0.0	0.0	31.5	28.4	0.0	0.0	30.0	30.4	1.6
5	7	8	39.2	41.5	39.9	37.2	40.0	38.4	39.4	40.8	0.6
5	7	10	39.4	42.0	0.0	42.0	35.6	38.7	39.5	40.7	1.2
5	8	9	27.2	29.0	26.1	28.6	29.9	26.2	27.8	29.3	0.6
5	8	11	29.3	23.8	0.0	26.4	30.6	0.0	27.5	29.0	1.5
5	9	10	32.7	33.2	33.4	28.9	38.8	33.9	33.5	33.2	1.3
5	10	11	0.0	25.7	26.7	0.0	0.0	0.0	26.2	26.4	0.5
5	11	12	0.0	25.1	0.0	0.0	0.0	0.0	25.1	17.7	5.0

6	0	8	0.0	103.4	101.3	97.1	0.0	98.1	100.0	100.1	1.5
6	0	10	0.0	20.2	0.0	0.0	0.0	0.0	20.2	15.4	4.5
6	0	12	0.0	137.1	132.3	133.0	0.0	130.7	133.3	133.0	1.4
6	1	7	38.2	36.5	34.4	36.2	35.6	37.9	36.5	35.2	0.6
6	1	9	38.4	41.2	41.4	34.8	34.1	36.1	37.7	37.7	1.3
6	1	11	37.5	40.7	36.3	38.1	42.2	38.4	38.9	38.5	0.9
6	1	13	0.0	0.0	0.0	21.6	0.0	0.0	21.6	19.1	4.6
6	1	15	0.0	0.0	23.7	0.0	0.0	0.0	23.7	23.5	4.9
6	2	8	71.3	75.9	72.7	70.1	72.2	73.6	72.6	72.0	0.8
6	2	10	120.6	124.7	122.8	120.7	118.9	119.7	121.2	123.3	0.9
6	2	12	76.1	77.6	80.1	75.1	74.9	0.0	76.8	76.9	1.0
6	2	14	0.0	0.0	69.2	69.5	68.7	69.5	69.2	69.5	0.2
6	3	7	69.1	74.6	0.0	69.8	71.1	74.6	71.9	71.0	0.9
6	3	9	30.2	30.2	24.9	25.0	26.0	22.7	26.5	28.7	1.2
6	3	11	24.8	0.0	20.8	0.0	19.2	0.0	21.6	21.0	1.6
6	3	13	0.0	0.0	24.7	21.7	0.0	26.3	24.2	24.1	1.4
6	4	8	120.6	129.7	128.9	121.3	122.6	122.8	124.3	124.1	1.6
6	4	10	32.2	35.2	28.9	30.4	31.3	0.0	31.6	30.9	1.1
6	4	12	89.9	94.2	98.2	91.8	92.3	91.2	92.9	91.1	1.2
6	5	7	35.5	36.1	34.3	37.2	31.1	32.9	34.5	33.4	0.9
6	5	9	33.3	37.1	33.6	36.1	35.1	0.0	35.0	35.8	0.7
6	5	11	33.5	31.8	32.8	31.7	32.6	37.6	33.3	32.7	0.9
6	6	6	151.7	151.4	0.0	0.0	0.0	0.0	151.5	158.5	0.2
6	6	8	79.7	82.6	0.0	76.9	76.5	0.0	78.3	79.3	1.3
6	6	10	78.9	82.4	85.1	83.6	83.4	87.1	83.1	81.8	1.0
6	6	12	88.9	94.9	92.3	93.4	91.9	89.0	90.8	91.0	1.3
6	6	14	0.0	0.0	59.2	61.1	62.3	0.0	60.9	59.9	0.9
6	7	7	24.7	31.1	26.2	26.0	26.7	0.0	26.9	28.2	1.1
6	7	9	22.3	24.0	0.0	22.2	0.0	25.5	23.5	25.0	0.8
6	7	11	27.9	34.2	31.0	36.1	32.6	30.8	32.1	31.4	1.2
6	7	13	0.0	0.0	0.0	0.0	25.4	25.7	25.6	23.7	0.1
6	8	8	56.1	54.0	58.0	53.7	55.1	58.1	55.8	54.3	0.8
6	8	10	44.1	43.8	44.0	42.8	45.4	43.7	44.0	43.8	0.3
6	8	12	83.4	84.1	81.5	80.3	83.2	87.1	83.3	81.7	1.0
6	9	9	25.5	26.2	25.4	0.0	29.7	28.3	27.0	26.6	0.8
6	10	10	56.5	62.4	61.4	59.7	59.4	60.1	59.9	61.0	0.8
6	10	12	88.4	90.9	86.6	83.8	0.0	0.0	87.4	88.2	1.5
7	1	8	57.0	55.9	53.3	52.5	53.6	54.8	54.5	55.5	0.7
7	1	10	36.4	35.8	36.9	31.3	36.3	38.4	35.8	36.1	1.0
7	2	11	0.0	0.0	21.6	0.0	0.0	0.0	21.6	14.2	4.6
7	3	8	45.5	47.3	47.2	45.9	43.7	44.4	45.7	45.9	0.6
7	3	10	34.4	38.6	34.7	34.2	33.6	32.4	34.6	33.8	0.8
7	3	12	22.4	24.7	26.5	0.0	0.0	0.0	24.6	25.2	1.2
7	4	9	0.0	0.0	22.5	22.6	24.7	0.0	23.3	23.5	0.7
7	4	13	0.0	0.0	0.0	23.4	0.0	26.2	24.8	20.1	1.4
7	5	8	27.9	29.0	29.5	32.8	28.7	30.8	29.8	31.0	0.7
7	5	10	24.7	28.5	29.8	29.2	27.7	0.0	28.0	28.3	0.9
7	5	12	26.6	29.6	26.0	28.9	23.0	0.0	26.8	27.1	1.2
7	6	9	34.6	38.0	33.8	37.4	36.1	0.0	36.0	36.9	0.8
7	6	11	26.5	27.9	26.8	28.6	30.7	30.4	28.5	27.4	0.7
7	6	13	0.0	0.0	0.0	24.6	0.0	0.0	24.6	21.1	5.0
7	7	8	29.5	29.1	0.0	27.4	27.9	0.0	28.0	28.2	0.6
7	7	10	34.9	38.3	27.8	36.6	35.3	32.8	34.3	35.3	1.3
7	7	12	29.1	33.3	30.5	29.5	27.8	26.2	29.3	29.0	0.9
7	8	9	22.2	26.2	26.5	25.8	22.6	23.1	24.4	24.0	0.8
7	8	11	39.0	44.9	42.9	41.9	39.3	0.0	41.6	43.5	1.1

7	9	10	0.0	27.9	23.2	23.5	0.0	24.3	24.7	23.5	1.1
7	10	11	0.0	0.0	0.0	27.4	0.0	0.0	27.4	28.1	5.2
8	0	10	0.0	46.1	45.7	45.3	0.0	46.6	45.9	43.5	0.3
8	0	12	0.0	90.9	86.6	87.4	0.0	83.1	87.0	87.5	1.6
8	0	14	0.0	0.0	79.8	78.8	0.0	0.0	79.3	78.2	0.5
8	1	9	42.5	42.0	42.0	38.9	40.8	44.6	41.8	41.1	0.8
8	1	11	0.0	23.8	24.8	0.0	26.4	0.0	25.0	26.3	0.7
8	1	13	0.0	0.0	34.4	31.4	30.5	28.9	31.3	30.2	1.2
8	2	10	113.5	117.0	117.3	109.9	111.5	114.2	113.9	114.7	1.2
8	2	12	22.4	0.0	24.6	22.5	0.0	22.2	22.9	19.7	0.5
8	2	14	0.0	0.0	0.0	110.9	0.0	0.0	110.9	110.8	10.5
8	3	9	40.0	38.7	37.6	40.2	39.6	41.1	39.5	40.1	0.5
8	3	11	25.7	25.2	29.4	25.7	25.1	31.1	27.0	26.0	1.0
8	3	13	0.0	0.0	0.0	0.0	21.6	21.4	21.5	17.9	0.1
8	4	10	70.8	70.6	72.0	65.1	71.2	71.9	70.3	70.8	1.1
8	4	12	56.1	60.0	57.5	55.3	60.3	55.7	57.5	57.1	0.9
8	5	9	30.3	29.8	28.7	31.6	29.5	30.4	30.0	30.3	0.4
8	5	11	23.9	0.0	20.8	21.8	0.0	23.7	22.5	21.0	0.8
8	6	10	94.1	99.3	98.5	98.0	99.7	103.0	98.8	98.5	1.2
8	6	12	38.2	42.5	40.6	40.7	40.1	39.7	40.3	37.2	0.6
8	7	9	22.8	22.4	0.0	23.8	0.0	24.4	23.3	22.8	0.5
8	7	11	25.2	0.0	34.0	29.4	25.1	32.3	29.2	29.3	1.8
8	8	8	61.8	62.7	0.0	61.8	0.0	0.0	62.0	62.8	0.3
8	8	10	76.4	83.2	81.0	78.9	84.2	83.1	81.3	81.5	1.0
8	8	12	51.5	51.6	0.0	0.0	0.0	0.0	50.5	49.6	1.0
8	9	9	35.0	38.8	36.2	31.8	36.8	33.7	34.6	34.6	1.1
8	9	11	0.0	0.0	0.0	23.0	0.0	0.0	23.0	23.5	4.8
8	10	10	63.5	63.2	61.7	61.2	0.0	0.0	62.4	63.2	0.6
8	10	12	47.4	0.0	0.0	0.0	0.0	0.0	47.4	44.4	6.9
9	1	10	22.2	22.1	0.0	20.0	0.0	0.0	21.0	18.9	0.5
9	1	12	25.7	29.3	26.8	0.0	24.5	28.7	27.0	25.7	0.9
9	3	10	37.8	37.1	42.1	40.9	41.3	40.9	40.0	41.5	0.8
9	4	13	0.0	0.0	23.4	23.6	0.0	0.0	23.5	20.9	0.1
9	5	10	43.7	42.2	41.1	38.2	39.3	43.4	41.3	41.3	0.9
9	5	12	0.0	0.0	0.0	0.0	0.0	23.9	23.9	20.5	4.9
9	6	11	29.6	27.4	31.1	28.9	24.7	31.7	28.9	30.0	1.0
9	7	12	28.6	26.4	0.0	0.0	0.0	0.0	27.5	24.5	1.1
9	8	11	0.0	0.0	0.0	0.0	25.8	0.0	25.8	25.2	5.1
9	9	10	24.8	26.5	0.0	0.0	0.0	0.0	25.6	22.1	0.8
10	0	12	0.0	107.3	105.6	108.3	0.0	108.2	107.4	109.6	0.6
10	1	11	0.0	0.0	25.7	25.4	26.7	23.6	25.4	25.9	0.6
10	1	13	0.0	0.0	0.0	0.0	0.0	25.3	25.3	25.1	5.0
10	2	12	51.0	49.9	50.9	48.0	48.5	51.8	48.7	50.4	1.4
10	3	11	35.7	34.4	30.9	31.2	34.9	33.3	33.4	34.5	0.8
10	4	12	110.6	110.1	111.5	105.1	109.2	109.9	109.4	111.1	0.9
10	6	12	56.8	63.5	0.0	0.0	60.6	59.1	60.0	60.3	1.4
10	8	12	70.5	0.0	0.0	0.0	0.0	0.0	70.5	72.2	8.4
11	1	12	29.5	0.0	0.0	0.0	25.3	25.8	26.9	26.3	1.3
11	6	11	26.6	26.1	0.0	0.0	25.1	0.0	25.9	23.2	0.4
12	2	12	37.3	35.8	0.0	0.0	37.3	42.4	38.2	37.5	1.4
0	1	0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0

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The Crystal Structure of $CuTeO_4$

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Crystals of $CuTeO_4$ are disordered. The structure has been determined in a unit cell with $a = 5{\cdot}500$ (2), b 10·327 (7), $c = 4{\cdot}704$ (2) Å, $\alpha = \beta = \gamma = 90{\cdot}0°$, $Z = 4$. Structural details have been obtained from a refinement in space group $P2_1/n$ ($R = 0{\cdot}048$), and the OD character of the structure is discussed in terms of idealized $[TeO_4]_n^{2n-}$ layers with the plane group symmetry $Pm(n)a$ ($R = 0{\cdot}054$). The Cu atoms have a distorted octahedral coordination of O atoms with Cu–O distances in the range 1·91–2·26 Å. The Te–O coordination is also octahedral; the octahedra are connected by corners forming $[TeO_4]_n^{2n-}$ layers. The Te–O bonds involving terminal and bridging O atoms are 1·87–1·91 and 1·91–2·02 Å respectively.

Introduction

The structures of some Cu^{II} tellurates(IV) have been determined: $CuTeO_3.2H_2O$ (Zemann & Zemann, 1962; Effenberger, 1977), $CuTeO_3$ (Lindqvist, 1972), $CuTe_2O_5$ (Hanke, Kupčik & Lindqvist, 1973), $Cu(NH_3)TeO_3.H_2O$ (Johansson & Lindqvist, 1977). However, information concerning Cu^{II} tellurates(VI) is limited to the structure of Cu_3TeO_6 (Falck, Lindqvist & Moret, 1978) which is built up from Cu^{2+} ions and TeO_6^{6-} ions of C_{3i} symmetry. In $CuTeO_4$ either a tetrahedral Te^{VI}–O coordination, as has been suggested for K_2TeO_4 (Tarte & Leyder, 1971), or, more probably, a polymerization of TeO_6 octahedra, as found in H_2TeO_4 (Moret, Philippot, Maurin & Lindqvist, 1974), is possible.

Experimental

Single crystals of $CuTeO_4$ were prepared by hydrothermal synthesis. From an aqueous solution of 0·5 *M* $CuSO_4$ and 0·5 *M* $Te(OH)_6$, kept at 650°C and 2000 bar for one week, single crystals of Cu_3TeO_6, $CuTeO_4$ and TeO_2 were obtained simultaneously. The $CuTeO_4$ crystals were very small plates. Slightly larger $CuTeO_4$ crystals could be prepared if the time for the hydrothermal synthesis was extended to two months, and the $Te(OH)_6$ concentration was increased to 1 *M*. Sone crystallographic data are given in Table 1.

Preliminary investigation with a Weissenberg camera

Table 1. *Crystallographic and powder data for* $CuTeO_4$ (MDO_1)

The cell parameters were refined with the program POWDER (Lindqvist & Wengelin, 1967). The powder data was obtained from a Siemens powder diffractometer.

Crystal habit: yellow plates
Space group: MDO_1: $P2_1n$ (MDO_2: $P\bar{1}$)
Plane group symmetry: $Pm(n)a$ (for $[TeO_4]_n^{2n-}$)

$a = 5{\cdot}500$ (2) Å	$V = 267{\cdot}2$ (3) Å
$b = 10{\cdot}327$ (7)	μ(Mo $K\alpha$) = 193·6 cm^{-1}
$c = 4{\cdot}704$ (2)	$\rho = 6{\cdot}345$ g cm^{-3}
$\beta = 90{\cdot}0$ (1)°	$m_f = 255{\cdot}15$
$\alpha = \gamma = 90°$	$Z = 4$

Powder data

h k l	$\sin^2\theta_o$	$\sin^2\theta_c$	d_o (Å)
0 2 0	0·02231	0·02229	5·161
1 0 1	0·04648	0·04650	3·576
1 1 1	0·05220	0·05207	3·374
1 2 1	0·06883	0·06879	2·935
2 1 0	0·08451	0·08415	2·652
0 4 0	0·08923	0·08916	2·581
1 3 1	0·09662	0·09665	2·480
2 2 0	0·10110	0·10087	2·425
0 0 2	0·10772	0·10742	2·349
0 4 1	0·11619	0·11601	2·262
2 2 1	0·12777	0·12772	2·157
2 3 0	0·12866	0·12873	2·149
0 2 2	0·12977	0·12971	2·140
1 1 2	0·13272	0·13264	2·116
2 4 0	0·16791	0·16774	1·881
2 0 2	0·18595	0·18600	1·788
0 4 2	0·19673	0·19658	1·738
3 0 1	0·20392	0·20366	1·707
3 1 1	0·20915	0·20923	1·686

showed that $CuTeO_4$ crystallizes with an OD structure (Dornberger-Schiff, 1966), diffuse intensity streaks being observed in the **b*** direction. The relative intensities of the streaks were very low compared with the intensities of the discrete reflections. Four different crystals were investigated, but all showed weak intensity streaks only in a few places in reciprocal space. This indicated that the stacking sequence corresponding to an ordered structure is relatively seldom broken.

Reflections corresponding to the unit cell given in Table 1 were measured, since the intensity effect of the continuous streaks could be considered as insignificant. The crystal used for data collection was mounted along [101] on a Pailred two-circle diffractometer. Graphite-monochromated Mo $K\alpha$ radiation was used, and the intensities were measured with the ω-scan procedure. The scan speed was 2·5° min^{-1} in ω, and the background was measured for 24 s at each end of the scan interval. Nine layer lines were explored out to $2\theta = 60°$. Reflections with $h + l = 2n + 1$, were very weak, and only 15 such reflections were strong enough to be considered observed. 403 reflections with $\sigma(I)/I < 0·3$ were regarded as being observed.

The intensities were corrected for Lorentz and polarization effects with the program *DATAP*1 (Lindgren, 1977) and for absorption with the program *DATAP*2 (Coppens, Leiserowitz & Rabinovich, 1965).

Structure determination

The observed reflections obey the symmetry and extinction rules of $P2_1/n$. The positions of the Te and Cu atoms were obtained from the Patterson function. In the successive electron density calculations, it was possible to find two sets of O atoms that satisfied the intensity data. One such model is shown in Table 2, and the same agreement ($R = 0·048$) was obtained if the refinement was carried out with all O atoms shifted by $(\frac{1}{2},0,\frac{1}{2})$. This indicated that the O atoms have higher symmetry than that inherent in $P2_1/n$. In fact the $[TeO_4]_n^{2n-}$ layer, as refined in $P2_1/n$, very closely obeys the plane group symmetry $Pm(n)a$. The O atom positions deviate 0·05–0·2 Å in the **a** direction. The

Table 2. *Structure solution refined in space group* $P2_1/n$

Equivalent positions: $\pm(x,y,z)$, $\pm(\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z)$; 15 positional and 7 thermal parameters varied; $R = \sum||F_o| - |F_c||/\sum F_o = 0·048$.

Atom	x	y	z	B (Å²)
Te	0·2963 (2)	0·2489 (6)	0·0166 (2)	0·23 (1)
Cu(1)	0			0·39 (5)
Cu(2)	$\frac{1}{2}$	0	$\frac{1}{2}$	0·55 (6)
O(1)	0·537 (4)	0·320 (2)	0·768 (4)	0·4 (2)
O(2)	0·535 (4)	0·173 (2)	0·267 (4)	0·7 (2)
O(3)	0·271 (3)	0·416 (1)	0·187 (3)	1·0 (2)
O(4)	0·271 (4)	0·088 (2)	−0·164 (4)	0·2 (2)

Table 3. *Constrained-layer model of the* $CuTeO_4$ *structure*

The $[TeO_4]_n^{2n-}$ layers have been constrained to the plane symmetry $Pm(n)a$. The Cu atoms only have the (n) glide plane in common with the $[TeO_4]_n^{2n-}$ layers, but their positions are completely determined by the translations r and s. The coordinate table is to be extended according to the (n) symmetry; equivalent positions: (x,y,z), $(\frac{1}{2}+x, -y, \frac{1}{2}+z)$.

Five positional and four thermal parameters were varied; $r = 0·054$.

	x	y	z	B (Å²)
Te(0)	0	0	0	B(Te)
O(01)	$\frac{1}{4}$	$y(01)$	$\frac{3}{4}$	B(01)
O(02)	$\frac{1}{4}$	$-y(01)$	$\frac{1}{4}$	B(01)
O(03)	0	$y(03)$	$z(03)$	B(03)
O(04)	0	$-y(03)$	$-z(03)$	B(03)
Cu(1)	$r/2$	$\frac{1}{4}$	$(1+s)/2$	B(Cu)
Cu(2)	$(1+r)/2$	$\frac{1}{4}$	$s/2$	B(Cu)
Te(1)	r	$\frac{1}{2}$	s	B(Te)
O(11)	$r+\frac{1}{4}$	$\frac{1}{2}+y(01)$	$s+\frac{3}{4}$	B(01)
O(12)	$r+\frac{1}{4}$	$\frac{1}{2}-y(01)$	$s+\frac{1}{4}$	B(01)
O(13)	r	$\frac{1}{2}+y(03)$	$s+z(03)$	B(03)
O(14)	r	$\frac{1}{2}-y(03)$	$s-z(03)$	B(03)

where $r = 0·4077$ (5); $s = -0·0331$ (6); $y(01) = 0·0740$ (11); $y(03) = 0·1635$ (13); $z(03) = 0·1702$ (32); B(Te) = 0·24 (1); B(Cu) = 0·54 (2); B(01) = 0·64 (15); B(03) = 0·93 (18)

geometry of this idealized layer is determined only by the three parameters $y_{O(01)}$, $y_{O(03)}$ and $z_{O(03)}$ (Table 3). The structure may then be described as built up of such layers stacked according to the translations $\mathbf{L}_0$, $\mathbf{L}_1 = \mathbf{L}_0 + [r,\frac{1}{2},s]$, $\mathbf{L}_2 = \mathbf{L}_1 + [-r,\frac{1}{2},-s] = \mathbf{L}_0 + [0,1,0]$, *etc.*, where r and s are refinable parameters. The coordinates of the Cu ions are completely determined by the translations (Table 3). The refinement of the constrained structure model (Table 3) gave an R of 0·054 with the least-squares program *BLOCK* (Lindgren, 1977). Because the number of positional parameters could be reduced from 15 in the $P2_1/n$ model (Table 2) to 5 in the constrained-layer model (Table 3) the parameter standard deviations were improved in spite of the increase in R. However, the R difference clearly indicates that the unconstrained $P2_1/n$ model is significantly better than the constrained-layer model, and the detailed description of the structure should thus refer to the $P2_1/n$ coordinates (Table 2).

The scattering factors of Cromer & Waber (1965) were used for Te and those of Doyle & Turner (1968) for Cu and O. Correction for the real part of the scattering was applied for Te and Cu (Cromer, 1965). The observations were weighted according to Cruickshank (1970) with $w(hkl) = [50·0 + F_o(hkl) + 0·01F_o(hkl)^2]^{-1}$.*

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33292 (4 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Discussion of the structure

Bond distances and angles, both for the unconstrained and the constrained, idealized model, were calculated with *DISTAN* (written by Zalkin, University of California), and are shown in Table 4.

The idealized layer model is useful for the description of possible disorder in the structure. The layer stacking, as described by the parameters in Table 3, is fully ordered with alternating translations $[r,\frac{1}{2},s]$ and $[-r,\frac{1}{2},-s]$. This arrangement thus represents a structure of maximum degree of order (Dornberger-Schiff, 1966), MDO_1. The two types of translations are chemically identical with respect to the contacts between the layers and the Cu coordination. It is therefore possible to build up another structure, MDO_2, in which each translation is positive, *i.e.* with layers $\mathbf{L}_0$, $\mathbf{L}_1 = \mathbf{L}_0 + [r,\frac{1}{2},s]$, $\mathbf{L}_2 = \mathbf{L}_0 + [2r,1,2s]$, *etc.* Schematic representations of the MDO_1 and MDO_2 structures are shown in Fig. 1.

Table 4. *Interatomic bond distances* (Å) *and angles* (°) *in* $CuTeO_4$

The columns refer to (*a*) the unconstrained $P2_1/n$ model and (*b*) the constrained $Pm(n)a$ layer model.

	(*a*)	(*b*)
Te–O(4)	1·87 (2)	1·88 (1)
Te–O(3)	1·91 (1)	1·88 (1)
Te–O(1)	1·91 (2)	1·97 (1)
Te–O(2)	1·93 (2)	1·97 (1)
Te–O′(1)	1·99 (2)	1·97 (1)
Te–O′(2)	2·02 (2)	1·97 (1)
Cu(1)–O(4)	2 × 1·91 (2)	2 × 2·05 (1)
Cu(1)–O(3)	2 × 2·12 (1)	2 × 2·17 (1)
Cu(1)–O(1)	2 × 2·26 (2)	2 × 2·14 (1)
Cu(2)–O(3)	2 × 1·94 (2)	2 × 1·99 (1)
Cu(2)–O(2)	2 × 2·11 (2)	2 × 2·22 (1)
Cu(2)–O(4)	2 × 2·22 (2)	2 × 2·05 (1)

O(1)–Te–O′(1)	177·7 (1·0)	O′(1)–Te–O(3)	91·2 (9)
O(1)–Te–O(2)	93·3 (9)	O′(1)–Te–O(4)	84·2 (9)
O(1)–Te–O′(2)	89·1 (8)	O(2)–Te–O′(2)	177·5 (1·2)
O(1)–Te–O(3)	87·7 (8)	O(2)–Te–O(3)	99·2 (8)
O(1)–Te–O(4)	86·5 (9)	O(2)–Te–O(4)	88·1 (9)
O′(1)–Te–O(2)	88·8 (9)	O′(2)–Te–O(3)	92·2 (9)
O′(1)–Te–O′(2)	88·8 (9)	O(3)–Te–O(4)	171·3 (8)

O(1)–Cu(1)–O(3)	96·0 (6)	,	85·0 (6)
O(1)–Cu(1)–O(4)	103·7 (8)	,	76·3 (8)
O(3)–Cu(1)–O(4)	90·7 (7)	,	89·3 (7)
O(2)–Cu(2)–O(3)	102·4 (7)	,	77·6 (7)
O(2)–Cu(2)–O(4)	94·3 (8)	,	85·7 (8)
O(3)–Cu(2)–O(4)	94·0 (7)	,	86·0 (7)

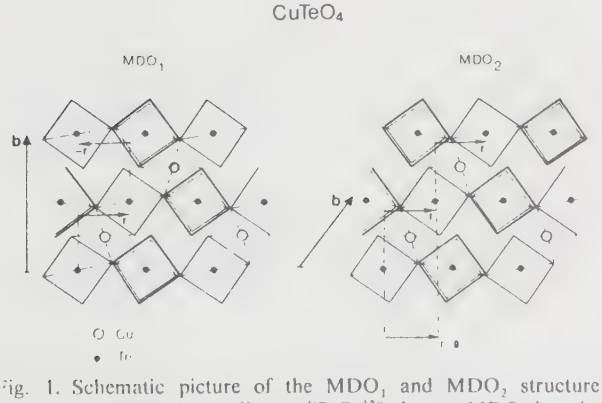

Fig. 1. Schematic picture of the MDO_1 and MDO_2 structure models showing three adjacent $[TeO_4]_n^{2n-}$ layers. MDO_2 has the unit cell dimensions $a = 5{\cdot}500$, $b = 5{\cdot}632$, $c = 4{\cdot}704$ Å, $\alpha = 90$, $\beta = 90{\cdot}0$, $\gamma = 66{\cdot}5°$.

The reciprocal lattices of the MDO_1 and MDO_2 structures coincide in the *h*0*l* plane, but the contribution of the MDO_2 structure in the crystal used for the structure determination was too small to appear as a significant increase in the F_o/F_c ratio for the *h*0*l* reflections, compared with the *hkl* reflections. Even in the other crystals investigated, the MDO_2 arrangement did not seem to occur to more than a few percent, although weak MDO_2 reflections could be detected from one of the crystals.

It should be noted that the refinement in $P2_1/n$ shows that the O atoms deviate slightly (0·05–0·15 Å) from the mirror plane in the plane group symmetry $Pm(n)a$, and $x_{O(01)} = x_{O(02)} = 0{\cdot}241$ and $x_{O(03)} = x_{O(04)} = -0{\cdot}025$, instead of $\frac{1}{4}$ and 0 respectively. In addition, the $[r,\frac{1}{2},s]$ translation does not hold strictly (in the $P2_1/n$ refinement results) for the *x* coordinates of the O atoms. However, the appearance of diffuse streaks in the **b*** direction confirms the OD character of the investigated crystals.

The results may be interpreted so that the Cu coordination of O atoms tends to distort the $[TeO_4]_n^{2n-}$ layers in a way which is more easily achieved in the MDO_1 than in the MDO_2 type of stacking sequence. In a related structure under investigation, $PbTeO_4$, similar disordered stacking occurs, but the two MDO structures occur to approximately the same extent.

The following discussion of the $CuTeO_4$ structural details refers to the unconstrained $P2_1/n$ model (Table 2).

Octahedral layers of composition $[TeO_4]_n^{2n-}$ have previously been found in Te_2O_5 (Lindqvist & Moret, 1973) and in H_2TeO_4 (Moret, Philippot, Maurin & Lindqvist, 1974). Both these structures are fully ordered and belong to the monoclinic space groups $P2_1$ and $P2_1/n$ respectively. The layers found in $CuTeO_4$ and Te_2O_5 can schematically be described in the same way (Fig. 2). The $Te-O_{bridge}$ bonds in $CuTeO_4$ are slightly longer than those in H_2TeO_4 and Te_2O_5, which have average values of 1·918 and 1·935 Å respectively. The $Te-O_{terminal}$ bonds of 1·87–1·91 Å in $CuTeO_4$ are in good agreement with values (1·83–1·91 Å) found in other tellurates(VI) (Lindqvist, 1973). In Te_2O_5 there are two different $Te-O_{terminal}$ bonds of 1·848 and 1·929 Å, as a result of the different connections with the interlayer Te(IV) atom.

Table 5. *Copper coordination in tellurates*

Compound	Type	Bond distances (Å) Cu–O	σ (Å)	Reference
(*a*) Te(IV)				
$CuTeO_3.2H_2O$	Square planar	1·93, 1·95, 1·96 1·97, 2·35, 3·37	0·01	1
$CuTeO_3$	Irregular	1·94, 1·97, 1·97 1·98, 2·38, 3·33	0·02	2
$CuTeO_3$(h.p.)	Square planar (distorted octahedral)	2 × 1·91, 2 × 2·06, 2 × 2·61	0·02	3
$Cu(NH_3)TeO_3.H_2O$	Square planar	1·950, 1·958, 1·960 1·998,* 2·602, 3·066	0·008	4
$CuTe_2O_5$	Square planar (distorted octahedral)	1·950, 1·952, 1·961 1·969, 2·305, 2·780	0·003	5
(*b*) Te(VI)				
Cu_3TeO_6	Square planar (distorted octahedral)	2 × 1·949, 2 × 2·031, 2 × 2·369	0·002	6
$CuTeO_4$	Octahedral	*cf.* Table 4	0·01	7

References: (1) Effenberger (1977). (2) Lindqvist (1972). (3) Philippot & Maurin (1976). (4) Johansson & Lindqvist (1977). (5) Hanke, Kupčik & Lindqvist (1973). (6) Falck, Lindqvist & Moret (1978). (7) This work.
* Cu–N bond distance.

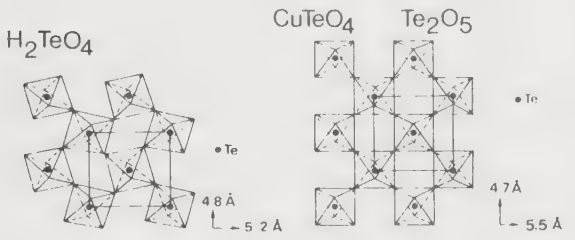

Fig. 2. A comparison of the $[TeO_4]_n^{2n-}$ layers found in H_2TeO_4, $CuTeO_4$ and Te_2O_5.

The Cu coordination in $CuTeO_4$ has been assumed to cause slight distortion of the $[TeO_4]_n^{2n-}$ layers. However, the packing of these layers mainly determines the geometry of the CuO_6 polyhedron, which is a distorted octahedron (Table 4). The Cu coordination in different tellurates is summarized in Table 5.

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References

Coppens, P., Leiserowitz, L. & Rabinovich, D. (1965). *Acta Cryst.* **18**, 1035–1038.

Cromer, D. T. (1965). *Acta Cryst.* **18**, 17–23.

Cromer, D. T. & Waber, J. T. (1965). *Acta Cryst.* **18**, 104–109.

Cruickshank, D. W. J. (1970). *Crystallographic Computing*, p. 195. Copenhagen: Munksgaard.

Dornberger-Schiff, K. (1966). *Lehrgang über OD-Strukturen*. Berlin: Akademie-Verlag.

Doyle, P. A. & Turner, P. S. (1968). *Acta Cryst.* A**24**, 390–399.

Effenberger, H. (1977). *Tschmerks Mineral. Petrogr. Mitt.* **24**, 287–298.

Falck, L., Lindqvist, O. & Moret, J. (1978).

Hanke, K., Kupčik, V. & Lindqvist, O. (1973). *Acta Cryst.* B**29**, 963–970.

Johansson, G. B. & Lindqvist, O. (1977). *Acta Cryst.* B**33**, 2418–2421.

Lindgren, O. (1977). Thesis. Univ. of Göteborg, Sweden.

Lindqvist, O. (1972). *Acta Chem. Scand.* **26**, 1423–1430.

Lindqvist, O. (1973). Thesis. Univ. of Göteborg, Sweden.

Lindqvist, O. & Moret, J. (1973). *Acta Cryst.* B**29**, 643–650.

Lindqvist, O. & Wengelin, F. (1967). *Ark. Kemi*, **8**, 179–187.

Moret, J., Philippot, E., Maurin, M. & Lindqvist, O. (1974). *Acta Cryst.* B**30**, 1813–1818.

Philippot, E. & Maurin, M. (1976). *Rev. Chim. Miner.* **13**, 162–174.

Tarte, P. & Leyder, F. (1971). *C. R. Acad. Sci. Sér. C*, **273**, 852–854.

Zemann, A. & Zemann, J. (1962). *Acta Cryst.* **15**, 698–702.

Observed and calculated structure factors for $CuTeO_4$.

h	k	l	Fo	Fc
0	0	2	177	183
0	0	4	174	177
0	1	2	23	-22
0	1	4	63	-54
0	1	6	54	-44
0	2	0	94	-89
0	2	2	52	-51
0	2	4	54	-59
0	3	2	37	33
0	3	4	49	47
0	3	6	44	42
0	4	0	197	223
0	4	1	75	70
0	4	2	238	238
0	4	3	23	-24
0	4	4	152	151
0	4	6	90	96
0	5	2	28	-32
0	5	6	61	-52
0	6	0	64	-65
0	6	2	62	-66
0	7	6	50	51
0	8	0	141	159
0	8	1	31	-28
0	8	2	185	187
0	8	4	123	116
0	8	6	94	91
0	9	6	51	-40
0	10	0	40	-40
0	10	2	53	-55
0	10	4	47	-40
0	12	0	134	154
0	12	2	112	107
0	12	4	100	102
0	14	0	48	-52
0	14	2	39	-33
0	14	4	48	-42
0	16	0	92	94
0	16	2	92	91
1	0	-5	70	71
1	0	-3	70	74
1	0	-1	68	68
1	1	-7	57	-66
1	1	-5	97	-98
1	1	-3	118	-121
1	1	-2	32	-26
1	1	-1	183	-186
1	1	2	30	26
1	1	3	96	-97
1	1	5	69	-71
1	2	-3	71	66
1	2	-1	130	130
1	2	1	151	162
1	2	3	147	149
1	2	5	102	112
1	2	7	84	89
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1	6	-1	101	101
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1	6	3	116	115
1	6	5	105	107
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1	7	-5	91	86
1	7	-3	98	95
1	7	-1	131	132
1	7	1	115	124
1	7	3	79	78
1	7	5	67	61
1	8	-5	52	54
1	8	-3	48	52
1	8	-1	40	38
1	9	-5	67	-70
1	9	-3	110	-106
1	9	-1	97	-102
1	9	1	80	-89
1	9	3	90	-94
1	10	-3	44	39
1	10	-1	69	66
1	10	1	83	89
1	10	3	94	96
1	11	-5	66	72
1	11	-3	76	78
1	11	-1	96	98
1	11	1	78	86
1	11	3	67	68
1	11	5	57	49
1	12	-5	54	45
1	12	-3	38	36
1	13	-5	56	-66
1	13	-3	70	-67
1	13	-1	80	-84
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1	14	3	68	69
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2	0	-6	69	-67
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2	1	4	75	78
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3	7	1	69	-68
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3	8	-3	95	93
3	8	-1	126	123
3	8	1	128	138
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3	8	5	107	105
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3	11	-1	60	-62
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6	5	2	76	67

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6	11	0	68	-68
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7	0	1	113	109
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7	4	-1	105	106
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7	8	-1	90	93
7	8	1	93	89
7	9	1	35	-41
8	1	-2	47	-50
8	1	0	66	-66
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8	6	-2	75	65
8	6	0	71	68
8	7	0	46	44

The Structure of Cubic $Te(OH)_6$

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Abstract $Te(OH)_6$, cubic, Fd3c, a = 15.705(3) Å, Z = 32, ϱ_x = 3.16 g cm^{-3}. The final R = 0.025 for 139 independent reflections. The structure is built up of $Te(OH)_6$ octahedra connected via hydrogen bonds. The Te-O distances are 1.913(6) Å (6x). The O-H---O bond lengths are 2.639(12) Å (6x) and 2.773(13) Å (6x).

Introduction The crystal structure of cubic telluric acid has previously been studied by Cohen-Addad (1971). Mahalaxmi (1968) solved the structure from film data and obtained a Te-O coordination distance of 1.88(3) Å. Cohen- Addad also tried to resolve the hydrogen atomic positions from a neutron powder investigation, but her data indicated disorder in the structure. A Te-O bond distance of 1.93 Å was given without any indication of standard deviation. The present refinement has been undertaken to resolve the oxygen coordination of Te(VI) in cubic $Te(OH)_6$ to an accuracy comparable with that of monoclinic $Te(OH)_6$ (Lindqvist, 1970; Lindqvist and Lehman, 1973).

The intensities were collected on a four-circle SYNTEX $P2_1$ diffractometer with graphite-monochromated Mo$K\alpha$ radiation. The crystal had the form of an octahedron with an edge of 0.12 mm. An $\omega/2\theta$ scan was used with scan intervals of 2.4-3.2° ($\Delta 2\theta$) and a scanning speed of 2.0-12.0 ° min^{-1}. The intensities were measured out to 2θ= 54° and 139 independent

reflections with $I/\sigma(I) > 3$ were used for the structure refinement. The background and integrated intensities were calculated with the Lehman-Larsen (1974) profile-analysis method (local program; Lindqvist and Ljungström, 1978). The data were corrected for Lorentz, polarization and absorption effects (program DATAPH; Coppens, Leiserowitz and Rabinovich, 1965); $\mu(MoK\alpha) = 62.08\ cm^{-1}$ (International Tables for X-ray Crystallography, 1962). The determination of the structure was started with the atomic positional parameters given by Mahalaxmi (1968). The final refinement included anisotropic temperature factors and an isotropic extinction parameter (LINUS; Coppens and Hamilton, 1970) and yielded an R of 0.025. The resulting positional and thermal parameters are given in Table 1.*

Discussion Interatomic distances and angles are given in Table 2. The structure of this phase of telluric acid is built up of discrete $Te(OH)_6$ octahedra. These are regular within the standard deviations and are held together by hydrogen bonds. The Te-O bond length within the octahedron agrees well with the bond length 1.916(5) Å (X-ray diffraction study; Lindqvist, 1970) and 1.909(1) Å (neutron diffraction study; Lindqvist and Lehman, 1973) in the monoclinic phase. The angles in monoclinic $Te(OH)_6$ vary significantly from the ideal value, i.e. in the range 87.60(6) - 92.08(7)°. The intermolecular O---O distances indicate that each $Te(OH)_6$ entity participates in six relatively strong hydrogen bonds (2.639(12) Å) and six weaker bonds (2.773(13) Å) involved with each molecule in $Te(OH)_6$. The average volume of each $Te(OH)_6$ molecule is 121.40 $Å^3$ in the cubic phase and 124.25 $Å^3$ in monoclinic $Te(OH)_6$. Preparation of suitable cubic $Te(OH)_6$ crystals for neutron diffraction work has been commenced in cooperation with Dr Jacques Moret, Montpellier, in order to be able to study the hydrogen bonds in detail.

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*Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32684 (7pp). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

REFERENCES

Cohen-Addad,C. Bull. Soc. Fr. Mineral. Cristallogr., 94 (1971)171-172

Coppens,P. and Hamilton,W.C. (1970) Acta Cryst. A26 (1970)71-83

Coppens,P. Leiserowitz,L. and Rabinovich,D. (1965) Acta Cryst. 18(1965) 1035-1038

Lindqvist,O. Acta Chem. Scand. , 24(1970)3178-3188

Lindqvist,O. and Lehman,M.S. Acta Chem.Scand.27(1973)85-95

Lindqvist,O. and Ljungström,E. (1978) to be published

Mahalaxmi,V. Thesis. Rensselaer Polytechnic Institute.(1968). Troy, New York. (No 69-2487, Ann Arbor, Michigan).

Table 1. Final positional parameters

	$\underline{x}$	$\underline{y}$	$\underline{z}$
Te	0	0	0
O	0.1402(4)	0.5425(4)	0.2809(4)

The anisotropic temperature factor is

$$\exp[-2\pi^2(\underline{h}^2\underline{a}^{*2}\underline{U}_{11} + \underline{k}^2\underline{b}^{*2}\underline{U}_{22} + \underline{l}^2\underline{c}^{*2}\underline{U}_{33} + 2\underline{hk}\underline{a}^*\underline{b}^*\underline{U}_{12} + 2\underline{hl}\underline{a}^*\underline{c}^*\underline{U}_{13} + 2\underline{kl}\underline{b}^*\underline{c}^*\underline{U}_{23}$$

	$\underline{U}_{11}$	$\underline{U}_{22}$	$\underline{U}_{33}$	$\underline{U}_{12}$	$\underline{U}_{13}$	$\underline{U}_{23}$
Te	0.00100(7)	0.00104	0.00104	-0.0001(1)	0	0
O	0.0013(3)	0.0018(3)	0.0016(3)	0.0004(2)	0.0002(2)	-0.000(

Table 2. Bond distances (Å) and angles (°) in cubic $Te(OH)_6$.

Te-O	O----O	O-Te-O
1.913(6) (6x)	2.639(12) (6x)	90.2(3)°
	2.773(13) (6x)	89.2(3)°

0	0	2	17	0	U
0	0	4	1560	1585	
0	0	6	20	0	U
0	0	8	1214	1222	
0	0	10	9	0	U
0	0	12	556	554	
0	0	14	22	0	U
0	0	16	537	536	
0	0	18	14	0	U
0	0	20	499	508	
0	0	22	15	0	U
0	0	24	363	374	
0	2	2	34	29	U
0	2	4	12	0	U
0	2	6	164	146	
0	2	8	8	0	U
0	2	10	102	107	
0	2	12	13	0	U
0	2	14	59	62	
0	2	16	26	0	U
0	2	18	25	5	U
0	2	20	24	0	U
0	2	22	17	-30	U
0	2	24	7	0	U
0	4	4	1041	1061	
0	4	6	18	0	U
0	4	8	1235	1213	
0	4	10	17	0	U
0	4	12	836	859	
0	4	14	30	0	U
0	4	16	678	677	
0	4	18	22	0	U
0	4	20	489	501	
0	4	22	32	0	U
0	4	24	356	334	
0	6	6	264	254	
0	6	8	15	0	U
0	6	10	91	77	
0	6	12	14	0	U
0	6	14	15	-48	U
0	6	16	22	0	U
0	6	18	60	-63	
0	6	20	14	0	U
0	6	22	16	-22	U
0	6	24	21	0	U
0	8	8	905	861	
0	8	10	23	0	U
0	8	12	717	717	
0	8	14	28	0	U
0	8	16	576	563	
0	8	18	19	0	U
0	8	20	449	444	
0	8	22	13	0	U
0	8	24	364	347	
0	10	10	92	87	
0	10	12	26	0	U
0	10	14	32	6	U
0	10	16	20	0	U
0	10	18	30	-23	U
0	10	20	20	0	U
0	10	22	20	-17	U
0	12	12	743	747	
0	12	14	27	0	U
0	12	16	563	555	
0	12	18	10	0	U
0	12	20	410	380	
0	12	22	27	0	U
0	14	14	43	-30	U
0	14	16	20	0	U
0	14	18	21	-13	U
0	14	20	38	0	U
0	16	16	430	424	
0	16	18	29	0	U
1	1	1	4	0	U
1	1	3	19	0	U
1	1	5	10	0	U
1	1	7	29	0	U
1	1	9	14	0	U
1	1	11	19	0	U
1	1	13	27	0	U
1	1	15	27	0	U
1	1	17	31	0	U
1	1	19	14	0	U
1	1	21	5	0	U
1	1	23	17	0	U
1	1	25	23	0	U
1	3	3	9	0	U
1	3	5	300	252	
1	3	7	362	-331	
1	3	9	78	67	
1	3	11	7	-20	U
1	3	13	29	-42	U
1	3	15	22	-5	U
1	3	17	15	-4	U
1	3	19	58	67	
1	3	21	32	-25	U
1	3	23	33	28	U
1	3	25	37	23	U
1	5	5	16	0	U
1	5	7	29	-23	U
1	5	9	36	-31	
1	5	11	115	-104	
1	5	13	79	-80	
1	5	15	51	54	
1	5	17	21	-5	U
1	5	19	43	23	U
1	5	21	48	-30	U
1	5	23	24	35	U
1	7	7	12	0	U
1	7	9	143	-139	
1	7	11	74	64	
1	7	13	78	-92	
1	7	15	46	-57	U
1	7	17	33	0	U
1	7	19	11	-20	U
1	7	21	17	-1	U
1	7	23	31	-11	U
1	9	9	13	0	U
1	9	11	13	-14	U
1	9	13	48	-53	
1	9	15	38	29	
1	9	17	42	31	
1	9	19	34	-50	
1	9	21	10	-4	
1	9	23	32	-15	
1	11	11	10	0	
1	11	13	26	-12	
1	11	15	16	3	
1	11	17	35	-32	
1	11	19	8	3	
1	11	21	14	-23	
1	13	13	30	0	
1	13	15	26	-10	
1	13	17	6	-15	
1	13	19	47	-29	
1	13	21	17	-22	
1	15	15	12	0	
1	15	17	36	13	
1	15	19	32	-15	
1	17	17	20	0	
2	2	2	1838	1713	
2	2	4	155	-140	
2	2	6	1166	1143	
2	2	8	17	-19	
2	2	10	1092	1077	
2	2	12	21	-17	
2	2	14	643	634	
2	2	16	32	33	
2	2	18	626	620	
2	2	20	45	41	
2	2	22	381	389	
2	2	24	5	12	
2	4	4	15	13	
2	4	6	136	-131	
2	4	8	61	54	
2	4	10	63	-54	
2	4	12	21	13	
2	4	14	16	36	
2	4	16	10	20	
2	4	18	30	40	
2	4	20	16	-10	
2	4	22	6	8	
2	4	24	20	-7	
2	6	6	1075	1068	
2	6	8	40	29	
2	6	10	977	968	
2	6	12	37	-36	
2	6	14	721	731	
2	6	16	21	14	
2	6	18	559	559	
2	6	20	14	30	
2	6	22	402	386	
2	6	24	23	1	
2	8	8	21	19	
2	8	10	18	-11	
2	8	12	19	-17	
2	8	14	8	-7	
2	8	16	21	-34	
2	8	18	20	-5	
2	8	20	16	-9	

| | | |

6	8	20	35	4	U
6	8	22	20	-33	U
6	10	10	660	658	
6	10	12	17	-8	U
6	10	14	552	550	
6	10	16	35	11	U
6	10	18	411	424	
6	10	20	25	10	U
6	10	22	345	349	
6	12	12	25	2	U
6	12	14	31	26	U
6	12	16	31	20	U
6	12	18	10	21	U
6	12	20	14	13	U
6	14	14	466	465	
6	14	16	24	12	U
6	14	18	366	359	
6	14	20	22	-3	U
6	16	16	18	-15	U
6	16	18	33	11	U
7	7	7	28	0	U
7	7	9	16	0	U
7	7	11	27	0	U
7	7	13	36	0	U
7	7	15	30	0	U
7	7	17	24	0	U
7	7	19	8	0	U
7	7	21	26	0	U
7	7	23	34	0	U
7	9	9	18	0	U
7	9	11	48	60	
7	9	13	24	49	U
7	9	15	14	0	U
7	9	17	49	40	
7	9	19	17	-8	U
7	9	21	14	-7	U
7	11	11	28	0	U
7	11	13	58	-71	
7	11	15	68	56	
7	11	17	23	3	U
7	11	19	21	6	U
7	11	21	27	4	U
7	13	13	16	0	U
7	13	15	23	0	U
7	13	17	27	10	U
7	13	19	12	-17	U
7	15	15	27	0	U
7	15	17	11	36	U
7	15	19	28	-11	U
7	17	17	12	0	U
8	8	8	769	784	
8	8	10	115	121	
8	8	12	663	673	
8	8	14	48	-62	U
8	8	16	513	538	
8	8	18	15	13	U
8	8	20	407	408	
8	8	22	62	-64	
8	10	10	22	2	U
8	10	12	20	16	U
8	10	14	27	-8	U
8	10	16	31	4	U
8	10	18	39	-15	U
8	10	20	38	-41	U
8	12	12	565	572	
8	12	14	25	-5	U
8	12	16	452	461	
8	12	18	37	32	U
8	12	20	357	349	
8	14	14	19	-7	U
8	14	16	33	36	U
8	14	18	27	-4	U
8	16	16	372	378	
8	16	18	29	-21	U
9	9	9	33	0	U
9	9	11	28	0	U
9	9	13	25	0	U
9	9	15	12	0	U
9	9	17	70	0	U
9	9	19	38	0	U
9	9	21	0	0	U
9	11	11	28	0	U
9	11	13	37	31	U
9	11	15	39	57	U
9	11	17	20	-33	U
9	11	19	23	-19	U
9	11	21	12	9	U
9	13	13	25	0	U
9	13	15	40	-26	U
9	13	17	33	14	U
9	13	19	12	-30	U
9	15	15	32	0	U
9	15	17	27	-38	U
10	10	10	662	676	
10	10	12	42	-40	U
10	10	14	539	540	
10	10	16	33	3	U
10	10	18	419	443	
10	10	20	40	26	U
10	12	12	6	-43	U
10	12	14	27	-5	U
10	12	16	17	-5	U
10	12	18	34	7	U
10	12	20	34	-15	U
10	14	14	401	396	
10	14	16	18	-10	U
10	14	18	356	355	
10	16	16	13	13	U
11	11	11	44	0	U
11	11	13	30	0	U
11	11	15	28	0	U
11	11	17	32	0	U
11	11	19	13	0	U
11	13	13	17	0	U
11	13	15	24	-1	U
11	13	17	41	-19	U
11	15	15	27	0	U
11	15	17	37	-23	U
12	12	12	433	419	
12	12	14	19	-29	U
12	12	16	360	361	
12	12	18	16	-1	
12	14	14	15	13	
12	14	16	30	11	

The Synthesis and Crystal Growth of $Te(OH)_6 \cdot 4H_2O$

by

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The binary system $Te(OH)_6$-H_2O has been studied between -5°C and room temperature. At temperatures under 10 °C it was possible to prepare crystals of the composition $Te(OH)_6 \cdot 4H_2O$. A single crystal of dimensions 11x18x12 mm and volume 1.3 cm^3 was grown by slow evaporation at 4 °C from a saturated solution.

Introduction

Many physical properties of tellurates may be explained by their structures. X-ray diffraction studies [1] show that tellurium(VI) oxygen compounds contain TeO_6 octahedra which are more or less distorted. The role of the hydrogen bonds in these deformations has already been discussed for H_2TeO_4 [2] and $Te(OH)_6$ [3]. The hydrate $Te(OH)_6 \cdot 4H_2O$ has been prepared for neutron diffraction and spectroscopic studies. The binary system $Te(OH)_6$ - H_2O has also been investigated in the temperature range -5 °C- 20 °C.

The existence of $Te(OH)_6 \cdot 4H_2O$ was reported as early as 1834 by Berzelius [4-5] and later by Staudenmaier [6] and Mylius [7]. The low evaporation rate at ~0°C and the precipitation of monoclinic telluric acid are factors which have complicated the previuos studies of $Te(OH)_6 \cdot 4H_2O$.

Preparation of $Te(OH)_6 \cdot 4H_2O$

21 g of $Te(OH)_6$mon were dissolved in 100 g distilled water at room temperature under stirring. The solution was then filtered through a glass filter No. 4 and the filtrate collected in a 250 ml beaker which was placed in a 1 litre vessel. A rubber gasket made this vessel airtight and it was removed to a cryostat K80DW containing methanol, in which the temperature could be adjusted to within 0.5 °C (Fig. 1). The temperature was held at 0 °C for 12 hours and no precipitate was formed. Lowering of the temperature to -15 °C caused the content to solidify but when the temperature was slowly raised to 0 °C the precipitate dissolved. It was possible to induce nucleation of $Te(OH)_6 \cdot 4H_2O$ in the following way: 5 ml of the clear solution were removed from the beaker in the cryostat and poured into a small crucible at 0 °C. The crucible was then slowly placed in a Dewar vessel containing N_2 (l). After solidification of the solution, the crucible with the temperature of N_2 (l) was replaced on the bottom of the 250 ml beaker in the cryostat at 0 °C. Nucleation then commenced on the surface of the cold crucible. Although the temperature of the contents in the beaker was maintained at 0 ° C the crystals formed did not dissolve.

An X-ray analysis showed that the microcrystalline phase formed consisted only of $Te(OH)_6 \cdot 4H_2O$.

Study of the binary system $Te(OH)_6$ - H_2O.

This study was carried out in another airtight flask of 1 l in which 700 g water and 200 g $Te(OH)_6$ (mon) were placed. When the acid had dissolved at 20 °C and had been filtered through a glass-filter (No 4) the flask was placed in the cryostat at 4 °C. No precipitate was formed after 12 hours but the hydrate could be made to precipitate by the addition of a few seed crystals.

Equilibrium between the solution and the hydrate was attained within less than 12 hours. The airtight glass flask was agitated vigorously for five minutes every four hours. The solubility was determined as follows:
After the solution had been allowed to stand for four hours a few ml were removed from the centre of the solution with a syringe of the same temperature as the liquid. Part of the content in the syringe was poured into a platinum crucible which was covered immediately with a plastic cover. The rest of the solution in the syring was poured into a pycnometer of well-defined volume. The crucible and the pycnometer were weighed. The cover was then removed from the platinum crucible and the solution evaporated at 70 °C for 12 hours. The solid residue of $Te(OH)_6$ was then heated slowly in air to 650 °C for 1 hour. After cooling, the residue of TeO_2 was weighed. It was possible to determine the weight percent of $Te(OH)_6$ (mon) and the density of the solution in equilibrium with the hydrate. Identical analyses were performed at different temperatures (Table 1).

The density of the solution is 1.18 g/cm^3 at 4 °C and 1.14 g/cm^3 at 0 °C. The results made it possible to draw a part of the phase diagram for the $Te(OH)_6$- H_2O system (Fig. 2). The eutectic temperature has been determined directly by thermal techniques.

Growth of a single crystal.

A solution of $Te(OH)_6$ was saturated at 4 °C and filtered through a glassfilter (No 4). This operation was carried out in a thermostated room at 4 ° ± 1 °C. Some small microcrystals of the hydrate were added to the solution which was allowed to evaporate slowly in a covered crystallization beaker. After 7 days crystals (1x2x4 mm) could be isolated. In order to grow a large single crystal one of these crystals was mounted on a nylon thread (Ø = 0.1 mm) and suspended in 500 ml of a saturated solution of $Te(OH)_6$ at 4 °C. The 1 l. beaker containing this solution was then transferred to a desiccator. The evaporation was carried out in two ways, either with the desiccator valve open or with a closed desiccator valve, the temperature being lowered by 0.25 °C/day in the latter case. In both cases single crystals of the shape shown in Fig. 3 and Fig. 4 were obtained.

Description and properties of the crystals.

In a saturated solution the crystals are completely transparent. They retain their appearance for some time in air at 4 °C but after a while a thin white layer forms on the surfaces (cf Fig. 4b) If the temperature is higher than + 10 °C the crystals turn opaque due to transformation to $Te(OH)_6$(mon).

In order to study the morphology of the hydrate at room temperature a mould was manufactured with a resin (Xantopren green, Bayer) which hardens quickly at 4 °C. An exact copy of the original crystal was then prepared with another resin (POLYESTER SODY 33). After 24 hours the resin had hardened at room temperature and a copy of the crystal was obtained (Fig. 4 a). The density of the crystal was determined

by filling the mould with mercury (d_{exp} = 2.4 g/cm^3, which is in good agreement with d_{calc} = 2.40 g/cm^{-3}, obtained from X-ray diffraction data). $Te(OH)_6 \cdot 4H_2O$ is tetragonal with cell parameters $\underline{a}$ = 10.790(4) and $\underline{c}$ = 7.108(3) Å (Fig. 3). This was confirmed by the X-ray diffraction data.

The formula $Te(OH)_6 \cdot 4H_2O$ has been confirmed by chemical analysis and by X-ray diffraction studies. The water of crystallisation can be removed by heating to 70 °C for several hours.

The crystal structure of $Te(OH)_6 \cdot 4H_2O$ is under investigation with both X-ray and neutron diffraction methods. The crystal used for collection of neutron data had the approximate dimensions 2 x 4 x 6 mm.

References

[1] O.Lindqvist. Thesis University of Göteborg (1973).

[2] J.Moret, E.Philippot, M.Maurin, O.Lindqvist Acta Cryst (1974) B30, 1813.

[3] O.Lindqvist, M.S.Lehman Acta Chem.Scand.27(1973) No.1.

[4] J.J.Berzelius Pogg. Ann 32 (1834) 26.

[5] J.J.Berzelius Ann.Chim. Phys.(2), 58 (1835) 43.

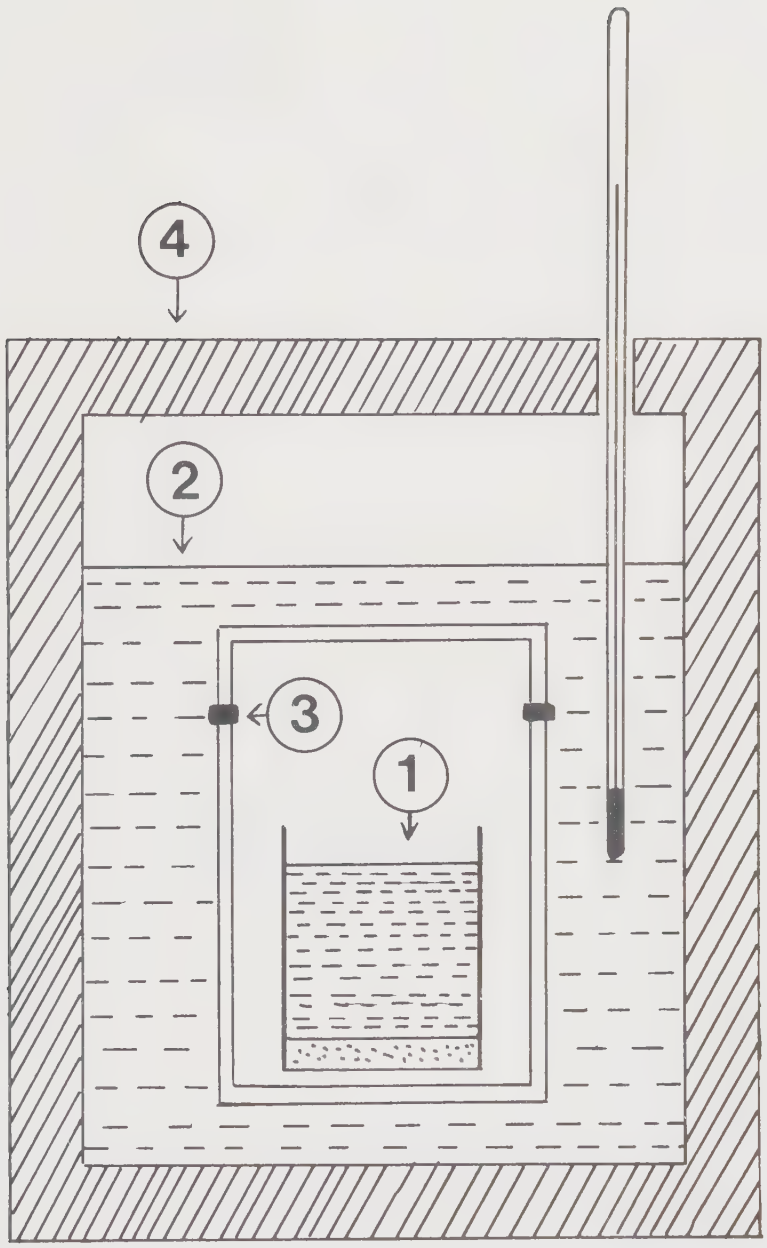
[6] L.Staudenmaier. Z.anorg.Ch. 10(1895) 192.

[7] F.Mylius Ber. 34 (1901) 2211, 2214.

Table 1

Temperature	Weight % $Te(OH)_6$	Remark
4℃	18.5	stable
2℃	16.8	stable
0℃	14.9	stable
-1.5℃	13.5	eutectic temperature
-2.5℃	12.4	metastable equilibrium

FIG1.



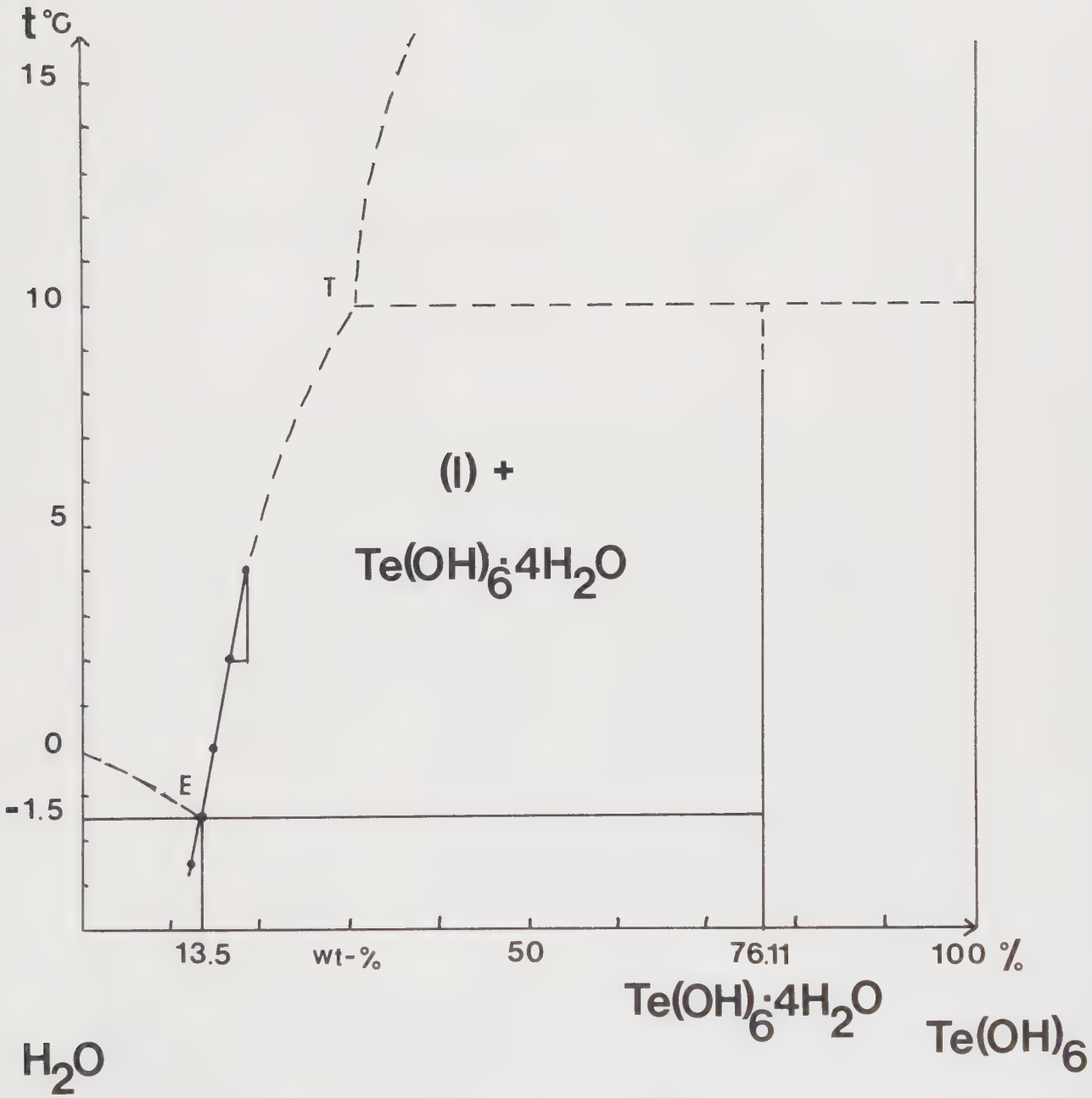
(1) Saturated solution of $Te(OH)_6 \cdot 4H_2O$

(2) CH_3OH

(3) Airtight vessel

(4) Cryostat

FIG 2.


t °C
15
10
5
0
-1.5
T
E
(l) +
Te(OH)6·4H2O
13.5
wt-%
50
76.11
100 %
H2O
Te(OH)6·4H2O
Te(OH)6

	$Te(OH)_6 \cdot 4H_2O$	a=10.790 Å c=7.108 Å space group: $I4_1/a$

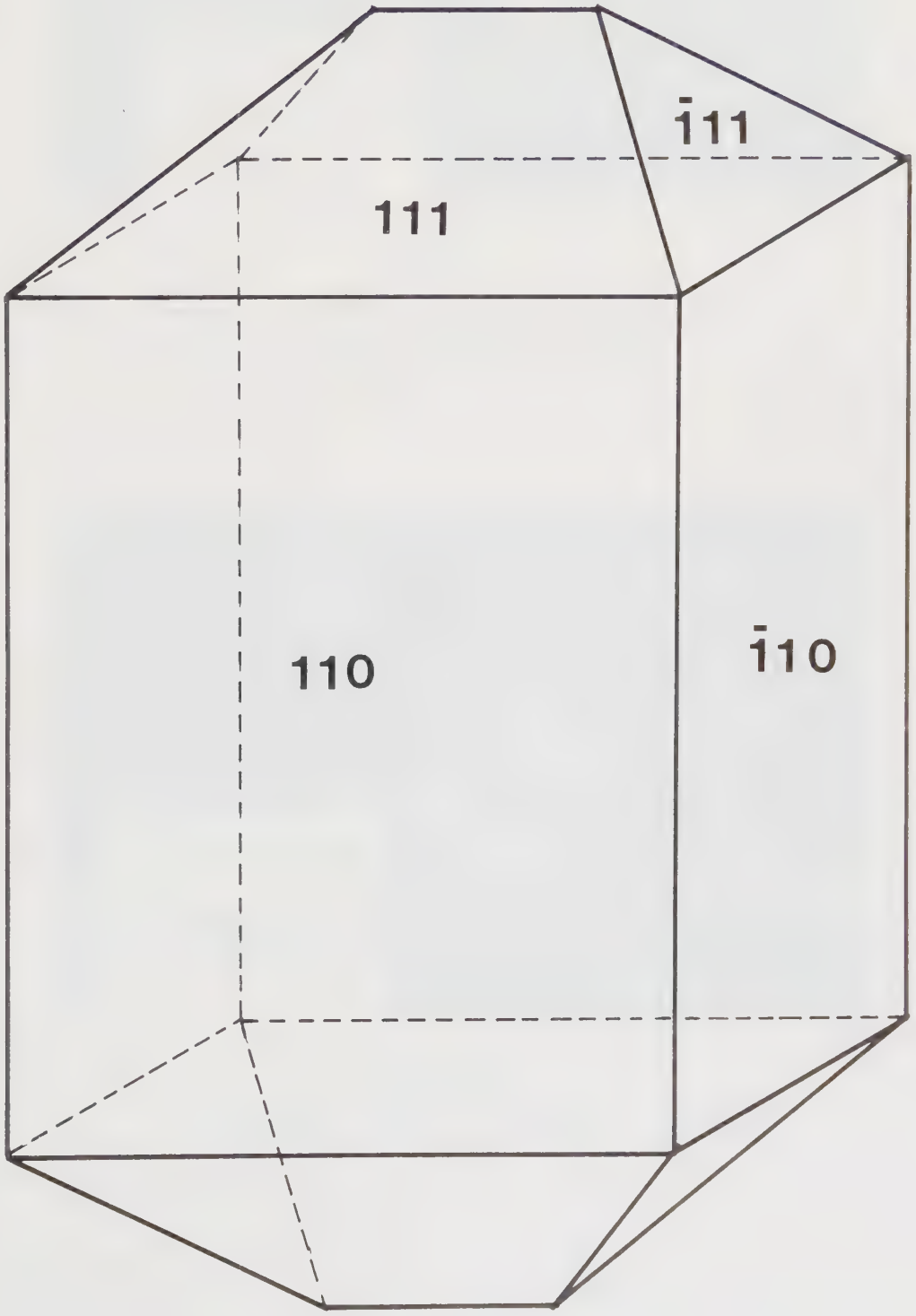


FIG 3

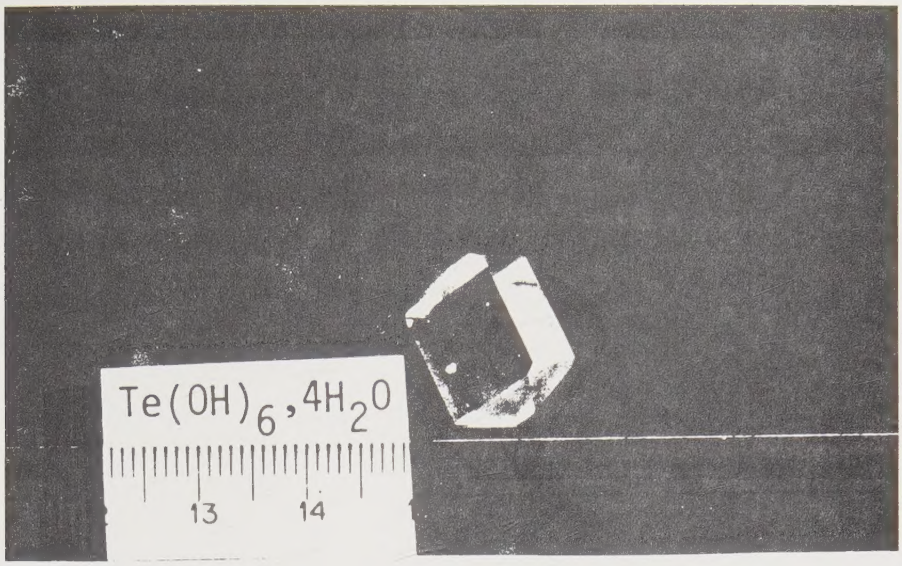


Fig 4a

A copy of the crystal made by the resin "Polyester SODY 33" (cf. Fig. 4b)

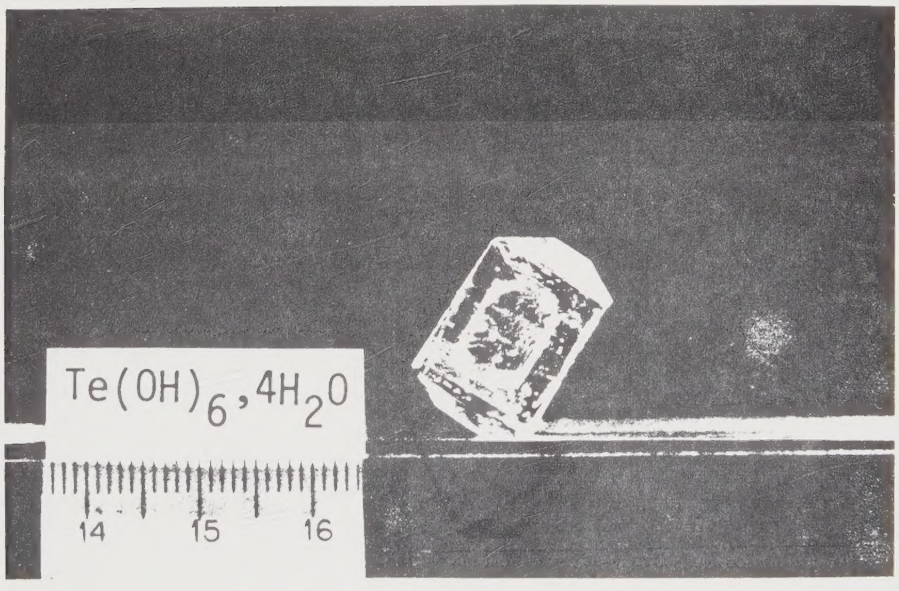


Fig 4b

The crystal after 20 minutes' exposure to air.